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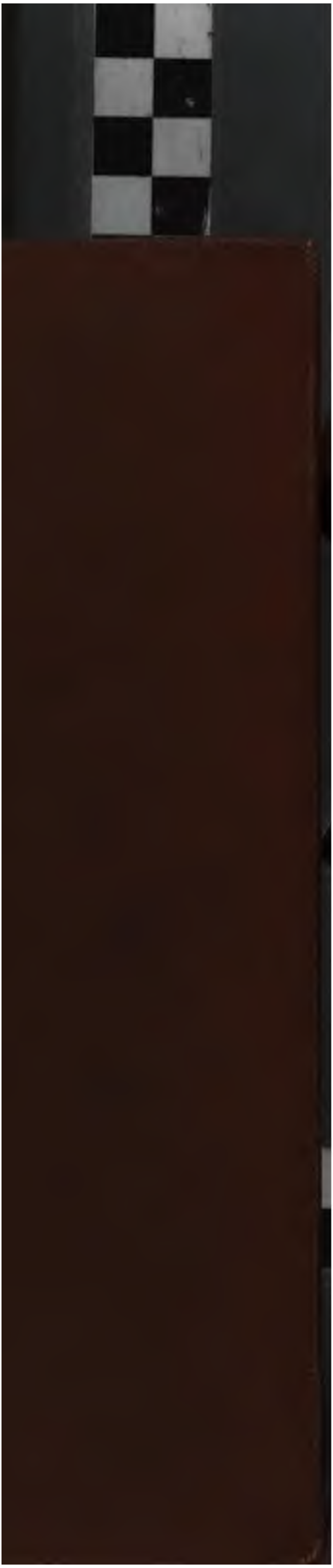

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TREATISE ON CHEMISTRY

BY

SIR H.enry E.nfield ROSCOE F.R.S. AND C.arl SCHORLEMMER F.R.S.

VOLUME III.

THE CHEMISTRY OF THE HYDROCARBONS AND THEIR DERIVATIVES,

OR

ORGANIC CHEMISTRY.

PART IV.

> "*Chymia, alias Alchemia et Spagirica, est ars corpora vel mixta, vel composita, vel aggregata etiam in principia sua resolvendi, aut ex principiis in talia combinandi.*"—STAHL, 1723.

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1888

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PREFACE TO VOL. III., PART IV.

THE Fourth Part of the Treatise on Organic Chemistry now presented to the public includes a description of the Aromatic Compounds containing seven atoms of Carbon, and, like the preceding part, forms a chapter complete in itself. The first portion is concerned with the Toluene Group, then come the Benzyl, Benzoyl, and Hydrobenzyl Groups, and lastly the Xylene Group of Eight Carbon Compounds.

CONTENTS.

TOLUENE GROUP . . . . . [illegible]
Toluene or Methylbenzene . . . [illegible]
Addition Products of Toluene . . [illegible]
Chlorine Substitution Products of Toluene . [illegible]
Monochlorotoluenes . . . . . [illegible]
Dichlorotoluenes . . . . [illegible]
Bromine Substitution Products of Toluene . [illegible]
Monobromotoluenes . . . . [illegible]
Dibromotoluenes . . . . . . [illegible]
Tribromotoluenes . . . . . [illegible]
Tetrabromotoluenes . . . . . . [illegible]
Iodine Substitution Products of Toluene [illegible]
Fluorine Substitution Products of Toluene . [illegible]
Nitro-Substitution Products of Toluene [illegible]
Mononitrotoluenes . . . . . . [illegible]
Dinitrotoluenes . . . [illegible]
Trinitrotoluenes . . . [illegible]
Chloronitrotoluenes . . . . [illegible]
Bromonitrotoluenes . . . [illegible]
Toluenesulphonic Acids . . [illegible]
Toluenemonosulphonic Acids . . 21
Toluenedisulphonic Acids . . . 22
Toluenetrisulphonic Acids . . [illegible]
Monohydroxytoluenes and Allied Bodies [illegible]
The Cresols . . . . [illegible]
Dihydroxytoluenes and Allied Bodies [illegible]
Homocatechol or Homopyrocatechin [illegible]
Orcinol . . . . . . [illegible]
Substitution Products of Orcinol . [illegible]
Chlorine Substitution Products . [illegible]
Bromine Substitution Products [illegible]
Iodine Substitution Products . . . . [illegible]
Nitro-Substitution Products . . . [illegible]
Cresorcinol . . . . . [illegible]
Toluquinol or Toluhydroquinone [illegible]
Toluquinone . . . . . [illegible]
Substitution Products of Toluquinone . [illegible]
Toluquinonoxime Compounds . . . . . . [illegible]
Trihydroxytoluenes . . . . [illegible]

PAGE
TOLUENE GROUP—*continued.*
Amido-Derivatives of Toluene 54
Amidotoluenes or Toluidines 54
Halogen Substitution Products of the Toluidines 67
Chlorotoluidines 68
Bromotoluidines 68
Iodotoluidines 68
Nitrotoluidines 69
Dinitrotoluidines 71
Diamidotoluenes or Tolylenediamines 72
Diazo-Derivatives of Toluene 74
Hydrazine-Derivatives of Toluene 75
Azo-Derivatives of Toluene 75
Phosphorus Derivatives of Toluene 83
Arsenic Derivatives of Toluene 84
Antimony Derivatives of Toluene 86
Boron and Silicon Derivatives of Toluene 87
Mercury Derivatives of Toluene 87
BENZYL GROUP 89
Benzyl Alcohol 89
Benzyl Ethers 94
Ethereal Salts of Benzyl 96
Substitution Products of Benzyl Alcohol and its Derivatives . . . 98
Sulphur Compounds of Benzyl 105
Selenium Compounds of Benzyl 109
Nitrogen Bases of Benzyl 110
The Benzylamines 110
Amido-Substituted Benzylamines 116
Substitution Products of the Benzylamines 118
Benzyl-Derivatives of the Acid-Amides and Allied Bodies . . . 121
Phosphorus Compounds of Benzyl 124
Arsenic Compounds of Benzyl 125
Silicon Compounds of Benzyl 127
BENZOYL GROUP 128
Benzaldehyde 129
Benzidene Compounds 136
Substitution Products of Benzidene Compounds 143
Benzoic Acid 151
Salts and Ethers of Benzoic Acid 160
Oxides of Benzoyl 166
Halogen Compounds of Benzoyl 168
Sulphur Compounds of Benzoyl 170
Nitrogen Compounds of Benzoyl 172
Hippuric Acid 181
Benzenyl Compounds 194
Benzonitril and its Derivatives 197
Benzimido-Ethers 200
Benzenylamidines 202
Benzenyloxime Compounds 207
Halogen-Substitution Products of Benzoic Acid 216
Monochlorobenzoic Acids 217
Dichlorobenzoic Acids 221
Trichlorobenzoic Acids 222

PAGE

BENZOYL GROUP—*continued.*

- Tetrachlorobenzoic Acid . . . 222
- Monobromobenzoic Acids . . . 223
- Dibromobenzoic Acids . . . 224
- Tribromobenzoic Acids . . . 225
- Mono-Iodobenzoic Acids . . . 225
- Monofluorbenzoic Acids . . . 226
- Nitro-Substitution Products of Benzoic Acid . . . 227
- Mononitrobenzoic Acids . . . 229
- Dinitrobenzoic Acids . . . 234
- Trinitrobenzoic Acid . . . 235
- Chloronitrobenzoic Acids . . . 236
- Bromonitrobenzoic Acids . . . 236
- Iodonitrobenzoic Acids . . . 237
- Monamidobenzoic Acids . . . 237
- Chloramidobenzoic Acids . . . 254
- Bromamidobenzoic Acids . . . 255
- Iodamidobenzoic Acids . . . 255
- Nitro-Amidobenzoic Acids . . . 255
- Dinitro-Amidobenzoic Acids . . . 257
- Diamidobenzoic Acids . . . 258
- Triamidobenzoic Acid . . . 260
- Diazo-Derivatives of Benzoic Acid . . . 260
- Hydrazinebenzoic Acids . . . 264
- Azo-Derivatives of Benzoic Acid . . . 265
- Monosulphobenzoic Acids . . . 268
- Disulphobenzoic Acids . . . 274
- Chlorosulphobenzoic Acids . . . 274
- Bromosulphobenzoic Acids . . . 274
- Nitrosulphobenzoic Acids . . . 275
- Amidosulphobenzoic Acids . . . 275
- Benzophosphinic Acid . . . 275
- Benzarsenic Acids . . . 277

HYDROXYBENZYL GROUP . . . 279
- Hydroxybenzyl Alcohols . . . 279
- Hydroxybenzaldehydes . . . 285
- Orthohydroxybenzaldehyde or Salicylaldehyde . . . 285
- Substitution Products of Salicylaldehyde . . . 292
- Metahydroxybenzaldehyde . . . 293
- Parahydroxybenzaldehyde . . . 294
- Hydroxybenzoic Acids . . . 297
- Orthohydroxybenzoic Acid or Salicylic Acid . . . 297
- Ethereal Salts of Salicylic Acid . . . 306
- Salicylic Ethers . . . 306
- Ethereal Salts of Salicylic Ethers . . . 307
- Substitution Products of Salicylic Acid . . . 313
- Metahydroxybenzoic Acid . . . 320
- Substitution Products of Metahydroxybenzoic Acid . . . 323
- Parahydroxybenzoic Acid . . . 326
- Substitution Products of Parahydroxybenzoic Acid . . . 334
- Substitution Products of Anisic Acid . . . 336
- Anisenyloxime Compounds . . . 339
- Dibenzanishydroxylamine . . . 341

PAGE

HYDROXYBENZYL GROUP—*continued.*

Benzanisbenzhydroxylamine . . . 341
Anisdibenzhydroxylamine . . . 341
Anisbenzanishydroxylamine . . . 342
Dianisbenzhydroxylamine . . . 342
Benzdianishydroxylamine . . . 342
Dihydroxybenzyl and Dihydroxybenzoyl Compounds . . . 343
Dihydroxybenzoic Acids . . . 350
Protocatechuic Acid or Orthodihydroxybenzoic Acid . . . 350
Symmetric Metadihydroxybenzoic Acid or α-Resorcylic Acid . . . 358
Asymmetric Metadihydroxybenzoic Acid or β-Resorcylic Acid . . . 359
Adjacent Metadihydroxybenzoic Acid or γ-Resorcylic Acid . . . 360
Hydroxysalicylic Acid or Paradihydroxybenzoic Acid . . . 361
Trihydroxybenzoic Acids . . . 363
Gallic Acid . . . 363
Pyrogallolcarboxylic Acid . . . 378
Phloroglucinolcarboxylic Acid . . . 380
Hydroxyquinolcarboxylic Acid . . . 380
Constitution of the Trihydroxybenzoic Acids . . . 381
Quinic Acid . . . 381
XYLENE GROUP . . . 386
The Xylenes or Dimethylbenzenes . . . 390
Substitution Products of the Xylenes . . . 392
Halogen Substitution Products of the Xylenes . . . 392
Nitro-Substitution Products of the Xylenes . . . 395
Xylenesulphonic Acids . . . 398
Hydroxy-Xylenes or Xylenols . . . 399
Dihydroxy-Xylenes . . . 402
Trihydroxy-Xylenes . . . 403
The Xyloquinones . . . 404
Amido-Derivatives of the Xylenes . . . 405
The Amidoxylenes or Xylidines . . . 405
Nitroxylidines . . . 408
Diamines and Triamines of the Xylenes . . . 409
Xylyl-Compounds . . . 410
Xylyl Alcohols . . . 411
Xylylamines . . . 412
The Tolualdehydes . . . 413
The Toluic Acids . . . 414
Hydroxytolualdehydes . . . 422
Hydroxytoluic Acids . . . 423
Dihydroxytolualdehydes . . . 427
Dihydroxytoluic Acids . . . 428
Xylylene Alcohols . . . 439
Hydroxymethylbenzoic Acids . . . 442
Aldehydes and Aldehydo-Acids . . . 447
The Phthalic Acids . . . 450
Phthalic Acid . . . 452
Addition Products of Phthalic Acid . . . 469
Halogen Substitution Products of Phthalic Acid . . . 471
Nitrophthalic Acids . . . 473
Amidophthalic Acids . . . 475
Sulphophthalic Acids . . . 476

PAGE

XYLENE GROUP—*continued.*
Isophthalic Acid or Metaphthalic Acid 479
Addition Products of Isophthalic Acid 481
Substitution Products of Isophthalic Acid 481
Terephthalic Acid 483
Addition Products of Terephthalic Acid 486
Substitution Products of Terephthalic Acid 488
Hydroxymethylhydroxybenzoic Acid 490
Aldehydohydroxybenzoic Acids 491
Hydroxyphthalic Acids 492
Hydroxymethyldihydroxybenzoic Acids 497
Aldehydodihydroxybenzoic Acids 502
Dihydroxyphthalic Acids 510
Trihydroxyphthalic Acids 519
Tetrahydroxyphthalic Acids 519

ORGANIC CHEMISTRY.

ORGANIC CHEMISTRY,

OR THE CHEMISTRY OF THE HYDROCARBONS AND THEIR DERIVATIVES.

PART IV.

TOLUENE GROUP.

TOLUENE OR METHYLBENZENE, $C_6H_5.CH_3$.

2017 This hydrocarbon was discovered by Pelletier and Walter in the oil obtained as a by-product in the manufacture of illuminating gas from the resin of *Pinus maritima*. They named it "retinaphtha" (*rétinnaphte*) and determined its composition accurately.[1] Shortly afterwards, Couerbe examined the liquid obtained by compressing the resin gas, and isolated from it, among other hydrocarbons, his *Heptacarbure quadrihydrique*, C_7H_4 ($C = 6$), which, in spite of some differences, he believed to be identical with retinaphtha.[2] Deville next obtained a hydrocarbon of the same composition by distilling the resin contained in Tolu balsam.[3] He named it benzoene (*benzoène*), because, in the first place, the balsam[4] from which it had been obtained contains benzoic acid; secondly, because, according to his formula, the hydrocarbon may be looked upon as the type of the

[1] *Ann. Chim. Phys.* lxvii. 269 ; *Pogg. Ann.* xliv. 8.

[2] *Ann. Chim. Phys.* lxix. 184 ; *Journ. Prakt. Chem.* xviii. 165.

[3] *Ann. Chim. Phys.* [3] iii. 168 ; *Journ. Prakt. Chem.* xxv. 336.

[4] Tolubalsam is obtained by incisions made in the bark of the *Myroxylon toluifera*, as mentioned by the Spanish physician Monardes in his *Historia de las cosas que se traen de nuestras Indias occidentales*, which first appeared complete in Seville in 1574, and in which he says that the balsam was collected by the Indians, in the district Tolu, in the neighbourhood of Carthagena (Flückiger and Hanbury, *Pharmacographia*).

benzoic series, and finally, because this name was similar to that of benzine (benzene), to which the substance bears the greatest resemblance. He considered, nevertheless, that benzoene was not identical, but isomeric with retinaphtha; Glénard and Boudault also considered the dracyl, which they had obtained, by the dry distillation of dragon's blood (from *Calamus draco*),[1] to be an isomeride of the former.

Hofmann and Muspratt then showed that it is identical with benzoene, for which somewhat unsuitable name Berzelius substituted that of toluol,[2] soon universally accepted, and still in use on the Continent, while in England it has been changed for the sake of consistency into toluene.

A complete investigation of toluene has proved that not only as regards its empirical formula, but in all its properties, it is the next higher homologue of benzene. Deville, as well as Glénard and Boudault, had already obtained from it nitrotoluene, $C_7H_7NO_2$ (nitrobenzoene, nitrodracyl), by the action of nitric acid, and Hofmann and Muspratt converted this by reduction into toluidine, $C_7H_7NH_2$, which resembles aniline very closely.[3]

Noad found that when cymene, $C_{10}H_{14}$, which is a constituent of Roman cumin-oil, is oxidized with nitric acid, toluic acid, $C_8H_8O_2$, the homologue of benzoic acid, is formed, and on distillation with caustic baryta decomposes into carbon dioxide and toluene, a reaction which corresponds exactly to the formation of benzene from benzoic acid.[4]

The relation of toluene to the benzoic series, which had already been pointed out by the French chemists, was experimentally proved by Cannizzaro, who found that benzyl alcohol, C_7H_7O, which is converted by oxidation into benzoic acid, undergoes a simultaneous oxidation and reduction when heated with concentrated alcoholic potash, benzoic acid and toluene being formed.[5]

Finally, Fittig and Tollens ascertained the constitution of toluene. These chemists obtained it synthetically by the action of sodium on a mixture of methyl iodide and bromobenzene,[6] by which reaction they not only proved that the product is methylbenzene, but pointed out a general and simple method by which the higher homologues can be prepared, and their constitutions determined.

---

[1] *Journ Prakt. Chem.* xxxi. 111 ; xxxiii. 466.

[2] *Jahresb.* xxii. 354.

[3] *Chem. Soc. Mem.* (1845) ii. 367.

[4] *Ibid.* iii. 421.

[5] *Ann. Chem. Pharm.* xc. 252.

[6] *Ibid.* cxxxi. 303.

Mansfield, whose results were subsequently confirmed by **Ritthausen**, was the first to prove that light coal-tar oils contain toluene and higher homologues as well as benzene[1] (Part III. p. 66). Toluene also occurs, together with xylene, in wood-tar; Cahours detected it in crude French pyroligneous acid,[2] and Völkel in the oil which comes over first in the distillation of beech-wood tar.[3] It is also found, together with its homologues, in several varieties of petroleum, such as that from Burmah (Rangoon tar),[4] as well as in the liquid obtained by the compression of the illuminating gas which is manufactured by heating the high boiling portions of petroleum, and has been used for lighting railway carriages.[5] It is obtained on the large scale from light coal-tar oil, and is chiefly employed in the colour industry.

Properties.—Toluene is a strongly refractive liquid, possessing a smell similar to that of benzene; it boils at 110·3° and does not solidify at −20°. Oxidizing agents convert it into benzoic acid. It combines with aluminium chloride forming the compound $Al_2Cl_6+6\,C_7H_8$, a thickish, orange-coloured liquid, which is violently decomposed by water with separation of toluene. A similar compound is formed with aluminium bromide.[6]

When toluene is heated with aluminium chloride to 200°, a portion of it is converted into paradimethylbenzene, paramethylethylbenzene, and metamethylethylbenzene, high boiling hydrocarbons being also formed, while benzene under the same conditions yields toluene, ethylbenzene and diphenyl.

In order to explain this remarkable reaction, Friedel and Crafts[7] assume that the following first takes place:

$$C_6H_6 + Al_2Cl_6 = C_6H_5Al_2Cl_5 + HCl$$
$$2C_6H_5Al_2Cl_5 + 2HCl = C_{12}H_{10} + 2Al_2Cl_6 + 2H_2.$$

The nascent hydrogen and the hydrochloric acid convert a portion of the benzene into methyl chloride and ethyl chloride, which then form toluene and ethyl benzene (Pt. III. p. 14.):

$$C_6H_5.Al_2Cl_5 + CH_3Cl = C_6H_5.CH_3 + Al_2Cl_6.$$

When toluene is employed, a similar reaction takes place; methyl chloride is, however, probably formed simultaneously, according to the equation:

$$C_6H_5.CH_3 + Al_2Cl_6 = C_6H_5Al_2Cl_5 + CH_3Cl.$$

---

[1] *Journ. Prakt. Chem.* lxi. 74.

[2] *Ann. Chem. Pharm.* lxxvi. 286.

[3] *Ibid.* lxxxvi. 335.

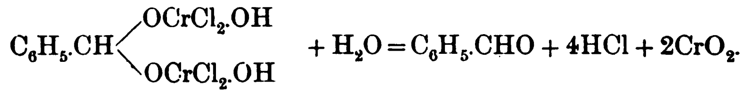
[4] *Journ. Prakt. Chem.* lxx. 300.

[5] Greville Williams, *Chem. News*, xlix. 197.

[6] Gustavson, *Ber. Deutsch. Chem. Ges.* xi. 2152.

[7] *Compt. rend.* c. 692.

When one part of chromium oxychloride is dissolved in ten parts of carbon disulphide, and the solution allowed to drop into a mixture of one part of toluene and ten parts of carbon disulphide, a chocolate-brown, crystalline precipitate of the empirical formula $C_7H_8+2CrO_2Cl_2$ is formed; this is soluble in glacial acetic acid, rapidly absorbs moisture, and is decomposed by water with formation of benzaldehyde and chromous chromate, showing that it is benzidenedichlorochromic acid:



$$C_6H_5.CH\left\langle\begin{array}{l}OCrCl_2.OH\\OCrCl_2.OH\end{array}\right. + H_2O = C_6H_5.CHO + 4HCl + 2CrO_2.$$

Alcohol and ether exert a similar action, ethyl chloride being formed in these cases. On heating the compound to 240°–245°, the chloride, $C_6H_5.CH\ (OCrOCl)_2$, is obtained; it has a darker colour and is more stable in moist air, but behaves towards water similarly to the acid.[1]

ADDITION PRODUCTS OF TOLUENE.

2018 *Dihydrotoluene*, C_7H_{10}, is obtained by heating toluene with phosphonium iodide to 350°, and is a liquid boiling at 105°–108°.[2]

Tetrahydrotoluene, C_7H_{12}, occurs in the distillation products of pine resin and colophonium, which are obtained on the large scale, and employed in the manufacture of varnishes, &c. The fraction boiling below 300°, which forms the smaller portion and is known as "resin spirit" or "essence of resin," is a mixture of fatty acids, aldehydes, paraffins, olefines, aromatic hydrocarbons and their addition products,[3] among which is tetrahydrotoluene. This substance is a liquid boiling at 103°–105°, and is converted by bromine into a crystalline bromide, $C_7H_6Br_6$. Tetrahydrotoluene combines with water to form a hydrate, $C_7H_{12}+2H_2O$, which crystallizes in long, white crystals, and, according to Renard, is identical with Anderson's colophonin, $C_7H_{14}O_2$, obtained by exposing resin spirit to the air for a long period;[4] while according to Tichborne, colophonin hydrate, $C_{10}H_{22}O_3 + H_2O$, is formed, and loses water on heating.[1]

---

[1] Étard, *Ann. Chim. Phys.* [5] xxii. 223.

[2] Baeyer, *Ann. Chem. Pharm.* clv. 271.

[3] Kelbe, *ibid.* ccx. 10; Kelbe and Bauer, *Ber. Deutsch. Chem. Ges.* xvi. 2559; Renard, *Ann. Chim. Phys.* [6], i. 223.

[4] *Chem. News*, xx. 76.

Hexhydrotoluene, C_7H_{14}, is prepared by heating toluene with a large excess of concentrated hydriodic acid to 280°,[2] and occurs in Baku petroleum[3] and in resin spirit (Renard). It is a liquid smelling like petroleum, boiling at 97°, and having a specific gravity of ·772 at 0°. A mixture of concentrated sulphuric and nitric acids does not attack it in the cold, but when hot oxidizes it completely.

CHLORINE SUBSTITUTION PRODUCTS OF TOLUENE.

2019 By the action of chlorine on toluene in the dark, Deville obtained *Benzoène monochloré*, C_7H_7Cl, as a thin liquid boiling at 170°,[4] whilst Cannizzaro found that the monochlorinated toluene obtained by the repeated distillation of toluene in a stream of chlorine, and boiling at 175°, is identical with benzyl chloride, as it can be readily converted into benzyl alcohol.[5] The same compound was also obtained by passing chlorine into toluene, but in this process an isomeric compound was frequently formed instead of the benzyl chloride, and this proved to be as stable as chlorobenzene. These enigmatical results were explained by Beilstein and Geitner,[6] who observed that the action of chlorine on toluene varies according to the temperature at which the chlorination is effected. Benzyl chloride alone is formed when the mixture is hot, while the stable chlorotoluene is formed when the process is conducted in the cold. As, however, heat is evolved by the action of the chlorine, the toluene, if used in large quantities and not carefully cooled, may become heated almost to the boiling point, benzyl chloride consequently being formed together with more or less chlorotoluene. The nature of this mixture can readily be exhibited by oxidizing it with chromic acid, the benzyl chloride being thus converted into benzoic acid, and the chlorotoluene into chlorodracylic acid

---

[1] *Chem. News*, xx. 38.

[2] Wreden and Znatowicz, *Ann. Chem. Pharm.* clxxxvii. 161.

[3] Beilstein and Kurbatow, *ibid.* xiii. 1818 ; see also xiv. 1620.

[4] *Ann. Chim. Phys.* [3], iii. 178.

[5] *Ann. Chem. Pharm.* xcvi. 246 ; *ibid.* cxli. 198.

[6] *Ibid.* cxxxix. 331.

(parachlorobenzoic acid), the acids being readily separated by means of the very great difference in their solubilities in water.

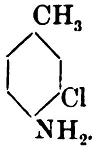
Beilstein and Geitner further found that chlorotoluene is more readily obtained by dissolving a little iodine in the toluene and then chlorinating, under which conditions no benzyl chloride is formed either in the cold or on heating.

As already mentioned (Part III. p. 17) all the hydrogen atoms of the aromatic group can be thus replaced by chlorine, whilst at the boiling point, in absence of iodine, substitution can only take place in the methyl group. By working alternately according to these two methods no octochlorotoluene can be obtained, the final products being pentachlorobenzidene chloride, $C_6Cl_5.CHCl_2$ and tetrachlorobenzal chloride, $C_6HCl_4.CCl_3$. If these be heated with antimony pentachloride in order to effect a further chlorination, they decompose with formation of hexchlorobenzene.[1]

MONOCHLOROTOLUENES, $C_6H_4Cl.CH_3$.

2020 *Orthochlorotoluene* is formed only in small quantities by the chlorination of toluene in the presence of iodine: it may, however, be readily obtained from orthotoluidine by means of the diazo-reaction.[2] It is a liquid boiling at 157°, which is oxidized by potassium permanganate to orthochlorobenzoic acid, whilst chromic acid solution produces complete oxidation.[3]

Metachlorotoluene is not formed by the action of chlorine on toluene; it has been prepared from metatoluidine, as well as from paratoluidine by converting this into acetoluide, $C_6H_4(CH_3)NH(C_2H_3O)$, chlorinating and decomposing the product by heating with caustic potash; the monochloroparatoluidine thus obtained is converted into the diazo-compound, and then decomposed with absolute alcohol;[4] chloroparatoluidine has, therefore, the following constitution:



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[1] Beilstein and Kuhlberg, *Ann. Chem. Pharm.* cl. 286.

[2] *Ibid.* clvi. 79; Gascorowski and Wayss, *Ber. Deutsch. Chem. Ges.* xviii. 1939.

[3] Emmerling, *Ber. Deutsch. Chem. Ges.* viii. 880.

[4] Wroblevsky, *Ann. Chem. Pharm.* clxviii. 199.

Hence we see that, on the chlorination of paratoluidine, the chlorine takes up the position adjacent to the basic group, and this also occurs in many other cases.

Metachlorotoluene is a liquid which boils at 156° and is converted by oxidation into metachlorobenzoic acid.

Parachlorotoluene is the chief-product of the action of chlorine on toluene in the presence of iodine.[1] It is advantageous to substitute molybdenum pentachloride for iodine, and to pass the chlorine through the mixture heated on the water-bath.[2] The product thus obtained does not solidify when cooled to a low temperature, since it contains various substances, such as the ortho-compound, &c., as impurities. If the parachlorotoluene be prepared from paratoluidine, it is obtained in a pure condition, and then boils at 160·5° and solidifies at 0° to a foliaceous mass, melting at 6·5°.[3] On oxidation it is converted into parachlorobenzoic acid.

Dichlorotoluenes, $C_6H_3Cl_2.CH_3$.

2021 When toluene is treated with sufficient chlorine in presence of iodine or molybdenum pentachloride, and the product purified by fractional distillation, a liquid boiling at 196° is obtained,[4] which, in spite of its constant boiling point, is not a definite compound, but a mixture of three dichlorotoluenes. If chlorine be passed into the vapour of the boiling liquid until no further action takes place, the hydrogen of the methyl group is replaced by chlorine and the corresponding dichlorobenzenyltrichlorides formed; on heating with water to 200° these are converted into three dichlorobenzoic acids:

$$C_6H_3Cl_2.CCl_3 + 2H_2O = C_6H_3Cl_2.CO_2H + 3HCl.$$

The formation of three dichlorotoluenes can readily be explained; the monochlorotoluene, which is first formed, consists chiefly of the para-compound, which can yield two isomeric dichlorotoluenes, whilst the third is formed from the orthochlorotoluene which is also present, though in smaller quantity.

The mixture appears to consist chiefly of asymmetric

[1] Beilstein and Geitner, *loc. cit.*

[2] Aronheim and Dietrich, *Ber. Deutsch. Chem. Ges.* viii. 1402.

[3] Hübner and Majert, *ibid.* vi. 794.

[4] Beilstein and Geitner; Beilstein and Kuhlberg, *Ann. Chem. Pharm.* cl. 313; Schultz, *ibid.* clxxxvii. 263. Aronheim and Dietrich.

dichlorotoluene, ($CH_3 : Cl : Cl = 1 : 3 : 4$), which yields the corresponding dichlorobenzoic acid on oxidation.

Dichlorotoluene hexchloride, $C_6H_3Cl_2(CH_3)Cl_6$, is obtained by the continued action of chlorine on toluene in the cold, and crystallizes from carbon disulphide in large prisms melting at 150°. When it is heated with alcoholic potash to 110°, *tetrachlorotoluene*, $C_6HCl_4.CH_3$, is formed; this compound is a liquid boiling at 280°–290°.[1]

The following substitution products have been obtained by the continued action of chlorine, assisted finally by the addition of antimony chloride :

		Melting-point.	Boiling-point.
α-Trichlorotoluene[2]	$C_6H_2Cl_3.CH_3(2 : 4 : 5)$	82°	230°
β-Trichlorotoluene[3]	$C_6H_2Cl_3.CH_3(2 : 3 : 4)$	41°	232°
Tetrachlorotoluene[4]	$C_6HCl_4.CH_3$	96°	276°·5
Pentachlorotoluene[5]	$C_6Cl_5.CH_3$	218°	301°.

BROMINE SUBSTITUTION PRODUCTS OF TOLUENE.

2022 All the theoretically possible compounds of this series are known.

MONOBROMOTOLUENES, $C_6H_4Br.CH_3$.

Orthobromotoluene is formed, together with a larger amount of parabromotoluene, by the bromination of toluene in the cold. The para-compound, which crystallizes out, is removed by pressing, and the liquid cooled in a freezing mixture, in order to remove as much of the solid as possible; the portion which remains liquid is then dissolved in alcohol and distilled, all the remaining parabromotoluene volatilizing in the vapour.[6] The para-compound may also be removed by means of sodium, which does not act upon the ortho-compound in the cold.[7] In order to effect this, the liquid is dissolved in benzene and allowed to stand over sodium for eight days; it is then distilled, and the fraction boiling between 170°—190° treated three or four times in the same way.[8]

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[1] Pieper, *Ann. Chem. Pharm.* cxlii. 304.

[2] Limpricht, *ibid.* cxxxix. 326 ; Schultz ; Aronheim and Dietrich ; Seelig, *Ber. Deutsch. Chem. Ges.* xviii. 420.

[3] Seelig.

[4] Limpricht ; Beilstein and Kuhlberg.

[5] Beilstein and Kuhlberg.

[6] Hübner and Jannasch, *Ann. Chem. Pharm.* clxx. 117.

[7] Luginin, *Bull. Soc. Chim.* iv. 514.

[8] Reymann, *ibid.* xxvi. 533.

Orthobromotoluene has also been prepared from orthotoluidine by means of the diazo-reaction.[1] It is a liquid, boiling at 182°—183° and is oxidized by dilute nitric acid to orthobromobenzoic acid, while chromic acid causes complete combustion.

Metabromotoluene has been obtained from metatoluidine and from parabromotoluidine (Wroblevsky).[2] It is a liquid which boils at 184·3° (Körner) and does not solidify at − 20°.

Parabromotoluene. The separation of this from orthobromotoluene is described above. It may be more rapidly effected by agitating the rectified mixture with half its volume of fuming sulphuric acid; the parabromotoluene separates out as a crystalline mass after some time.[3] It boils at 182·5°,[4] and is deposited from an alcoholic solution in rhombic crystals melting at 28·5°. When given to a dog, it appears in the urine as parabromohippuric acid and parabromobenzoic acid. When it is treated with chromium oxychloride, bromobenzidenedichlorochromyl chloride, $C_6H_4Br.CH(OCrOCl)_2$ is formed as a brown precipitate which is decomposed by water with formation of parabromobenzaldehyde (Étard).

DIBROMOTOLUENES, $C_6H_3Br_2.CH_3$.

2023 These have been prepared from the monobromotoluidines by the replacement of the amido-group by bromine, and from the dibromotoluidines by the replacement of the amido-group by hydrogen.[5] The first compound in the following list has also been obtained by the direct bromination of toluene; the process goes on much more rapidly in the presence of iodine and in the sunlight.[6]

CH_3 :	Br :	Br		Melting-point.	Boiling-point.
1	3	4	liquid, does not solidify at − 20°	—	240°
1	2	6	„ „ „ „	—	246°
1	2	5	„ „ „ „	—	236°
1	2	4	„ „ „ „	—	—
1	2	3	solid	28°	—
1	3	5	long needles	39°	246°

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[1] Wroblevsky, *Ann. Chem. Pharm.* clxviii. 171.

[2] See also Grete, *ibid.* clxxvii. 231.

[3] Hübner and Wallach, *Ann. Chem. Pharm.* cliv. 293.

[4] Hübner and Post, *ibid.* clxix. 6.

[5] Wroblevsky, *ibid.* clxviii. 161; Neville and Winther, *Ber. Deutsch. Chem. Ges.* xiii. 962; xiv. 417.

[6] Jannasch, *Ann. Chem. Pharm.* clxxvi. 286.

On treatment with nitric acid they yield all the mononitro-compounds which are theoretically possible; most of these compounds crystallize in needles.

TRIBROMOTOLUENES, $C_6H_2Br_3.CH_3$

These are obtained in a similar manner to the preceding compounds.[1]

CH_3 :	Br :	Br :	Br :		Melting-point.	Boiling-point.
1	3	4	5	crystals	88°—89°	—
1	2	3	4	crystals	46°	—
1	2	4	6	long needles . .	66°	290°
1	2	3	5	flat needles . .	52°·5	—
1	2	4	5	long needles . .	112°	—
1	2	5	6	flat needles . .	58°—59°	—

TETRABROMOTOLUENES, $C_6HBr_4.CH_3$.[2]

CH_3 :	Br :	Br :	Br :	Br :		Melting-point.	Boiling-point.
1	2	3	4	5	thin needles .	111°—111°·5	—
1	2	3	5	6	fine needles .	116°—117°	—
1	2	3	4	6	crystals . . .	105°—108°	—

Pentabromotoluene, $C_6Br_5.CH_3$, is formed when toluene is allowed to drop into bromine which is free from chlorine and to which some aluminium bromide has been added, as well as by replacing the amido-group of tetrabromotoluidine by bromine (Neville and Winther). It crystallizes from benzene in long needles, melting at 282°—283°.

When toluene is treated with an excess of bromine containing iodine, and the temperature finally allowed to rise to 350°—400°, hexbromobenzene and tetrabromomethane are formed, the latter being, however, for the most part converted into the former.[3]

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[1] Wroblevsky ; Neville and Winther, *loc. cit.*

[2] *Ibid.*

[3] Gessner, *Ber. Deutsch. Chem. Ges.* ix. 1508.

IODINE SUBSTITUTION PRODUCTS OF TOLUENE.

Only the mono-iodotoluenes, $C_6H_4I.CH_3$, which are obtained from the toluidines, are known.[1]

		Boiling-point.	Melting-point.
Ortho-iodotoluene	liquid . .	204°	—
Meta-iodotoluene	„ . .	204°	—
Para-iodotoluene	plates . .	211°·5	35°

FLUORINE SUBSTITUTION PRODUCTS OF TOLUENE.

Fluotoluene, $C_6H_4F.CH_3$, is formed when the diazo-compound obtained from paramidotoluenesulphonic acid is decomposed with strong hydrofluoric acid. It is a liquid smelling of bitter almonds, and boiling at 114°.[2]

NITRO-SUBSTITUTION PRODUCTS OF TOLUENE.

MONONITROTOLUENES, $C_6H_4(NO_2)CH_3$.

2024 By dissolving toluene in fuming nitric acid and precipitating with water, Deville obtained nitrotoluene (*protonitrobenzoène*) as a colourless liquid boiling at 225°, and possessing a smell of bitter almonds and a very sweet, somewhat biting taste. This compound was then repeatedly prepared by many chemists, who confirmed Deville's statements.

These circumstances served to render the following observations of Jaworsky the more remarkable; this chemist found that when nitrotoluene is dissolved in fuming nitric acid, and water added to the solution, a precipitate is formed which separates from a hot, alcoholic solution in lustrous crystals melting at 54°

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[1] Beilstein and Kuhlberg, *Ann. Chem. Pharm.* clviii. 147 ; Körner, *Zeitschr. Chem.* clxxxviii. 327.

[2] Paterno and Oliveri, *Gaz. Chim. Ital.* xiii. 533.

and which, boiling without decomposition at 238°, has exactly the same composition as nitrotoluene. He obtained the same compound by continuing the distillation of the liquid nitrotoluene to 240°; the residue, which solidified on cooling, was identical with the product obtained by the other method. He concluded from these experiments that pure nitrotoluene is a solid body, the crystallizing power of which is usually destroyed by liquid impurities, these also having the power of lowering the boiling point.[1]

These observations were confirmed by other chemists and were even taken advantage of commercially, for well crystallized nitrotoluene was manufactured on the large scale in Paris in 1867. Alexejew confirmed Jaworsky's view by obtaining the same azotoluene from the solid as from the liquid nitrotoluene.[2] He also found that the solid compound is converted by reduction into a solid toluidine,[3] which could not be obtained from the liquid compound.

Kekulé, who also investigated these facts, confirmed the above observation, and showed in addition that the solid nitrotoluene is more readily oxidized to paranitrobenzoic acid and gives a better yield than the liquid; the lower boiling portion of the latter yielded a liquid toluidine containing aniline, and he therefore considered it probable that the substance which had up to that time been looked upon as nitrotoluene was a mixture of nitrobenzene and nitrotoluene.[4]

Rosenstiehl, however, made the discovery that the ordinary liquid toluidine is a mixture of the solid with the isomeric pseudotoluidine,[5] and that, consequently, two nitrotoluenes are formed by the nitration of toluene.[6] In order to decide the question whether toluene itself is a mixture of two isomeric hydrocarbons, he investigated the behaviour of samples of toluene from various sources towards nitric acid. He took some which had been previously exposed to a red heat, and some which he had obtained by the decomposition of xylene, $C_6H_4(CH_3)_2$, at a high temperature. He also investigated toluene synthetically prepared, and that obtained from Tolu balsam. In all cases he obtained the two toluidines. Finally, Berthelot reduced these by heating with hydriodic acid and obtained one and the same toluene.[7]

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[1] *Zeitschr. Chem.* 1865, 222.

[2] *Ibid.* 1866, 269.

[3] *Bull. Soc. Chim.* vii. 376.

[4] *Zeitschr. Chem.* 1867, 225.

[5] *Ibid.* 1868, 557.

[6] *Ibid.* 1869, 190.

[7] *Ibid.*

Hence the supposition appeared not improbable that the lower boiling portion of ordinary nitrotoluene would be an isomeride of the solid compound, which yields the pseudotoluidine; Rosenstiehl, however, singularly enough, did not investigate this point, and it was reserved for Beilstein and Kuhlberg to answer the question. These chemists had already prepared the liquid β-nitrotoluene from dinitrotoluene, by converting the latter into nitrotoluidine, $C_6H_3(NH_2)(NO_2).CH_3$, by partial reduction with ammonium sulphide, and then replacing the amido-group by hydrogen. They then found that this nitrotoluene, which they called metanitrotoluene, but which is now known as the ortho-compound, forms the more volatile portion of crude nitrotoluene and can be separated from the solid paranitrotoluene by repeated careful fractional distillation.[1]

A small quantity of metanitrotoluene is formed, together with the ortho- and para-compounds, by the action of fuming nitric acid on toluene.[2] The relative quantities of the two chief products which are formed depend upon the concentration of the acid, and the temperature at which the nitration is effected. When a very concentrated acid is employed and the temperature allowed to rise, paranitrotoluene is chiefly obtained, while the yield of the ortho-compound is greatly increased by employing a weaker acid and cooling the mixture well.

The nitrotoluenes are manufactured on the large scale, by mixing 10 parts of toluene with 11 parts of nitric acid of specific gravity 1·22 and 1 part of sulphuric acid of specific gravity 1·33 with continual agitation, in the apparatus used for the manufacture of nitrobenzene; the mixture is then either cooled or kept warm according to the product desired. The crude product is washed with water and caustic soda solution, freed from unattacked toluene by distillation with steam, and then distilled with super-heated steam. The distillate is then repeatedly fractionated; the larger portion of the fraction distilling above 230° solidifies on cooling, and the crystals, after purification by draining and pressing, yield pure paranitrotoluene on distillation; the fraction boiling between 222°—223° consists chiefly of orthonitrotoluene, while the intermediate fractions contain some of the meta-compound.

Orthonitrotoluene is obtained pure when the amido-group of the isomeric nitrotoluidines, which contain the nitroxyl in the ortho-relation to the methyl group, is replaced by hydrogen: this is best effected by heating the compound with alcohol saturated with nitrogen trioxide. It is a liquid which boils at 223°, does not solidify at – 20°, and has a specific gravity of 1·163 at 23·5°.

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[1] *Ann. Chem. Pharm.* clv. i.

[2] Monnet, Reverdin and Nölting, *Ber. Deutsch. Chem. Ges.* xii. 445.

Metanitrotoluene is prepared by the same method from the corresponding nitrotoluidine. It solidifies in a freezing mixture to crystals which melt at 16°; it boils at 230°—231°, and has a specific gravity of 1·168 at 22°.[1]

Paranitrotoluene boils at 238°, and on the gradual evaporation of its alcoholic or ethereal solution separates in large, thick rhombic crystals melting at 54°.

DINITROTOLUENES, $C_6H_3(NO_2)_2,CH_3$.

2025 *Ordinary Dinitrotoluene* ($CH_3 : NO_2 : NO_2 = 1 : 2 : 4$) was obtained by Deville, and is formed by the further nitration of ortho- and para-nitrotoluene. In order to prepare it, toluene is run into fuming nitric acid, without any special cooling, until oily drops separate out; the mixture is then allowed to cool, and an equal volume of sulphuric acid gradually added, the whole being then boiled for half an hour, poured into snow, and the precipitate recrystallized from hot carbon disulphide.[2] It crystallizes in long, monoclinic needles, which melt at 72°, are only slightly soluble in cold alcohol, and still less so in cold carbon disulphide, but dissolve readily in boiling benzene.

In the manufacture of dinitrotoluene on the large scale, a liquid by-product is obtained, which was formerly considered to be an isomeric dinitrotoluene.[3] According to Claus and Becker it is a mixture of ordinary dinitrotoluene, orthodinitrotoluene, and orthomononitrotoluene.[4] Limpricht found that 1 : 2 : 5 dinitrotoluene is also contained in it; he did not isolate this compound but converted it into the corresponding nitrotoluidine.[5] Nölting and Witt, who examined a larger quantity of the by-product, obtained from it by distillation in a rapid current of steam 40 per cent. of mononitrotoluenes, consisting of almost equal parts of the para- and meta-compounds, the ortho-compound being present only in very small amount. Although metanitrotoluene is only formed to a small extent by the nitration of toluene, its presence in comparatively large quantities in the mixture can be readily understood, as it resists the further action of nitric acid much more strongly than its isomerides; it therefore accumulates in the by-product, while the more readily attacked ortho-compound almost disappears.[1]

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[1] Beilstein and Kuhlberg, *Ann. Chem. Pharm.* clviii. 348.

[2] *Ibid.* clvi. 13.

[3] Rosenstiehl, *Ann. Chim. Phys.* [4] xxvii. 407. Cunerth, *Ann. Chem. Pharm.* clxxii. 222.

[4] Claus and Becker, *Ber. Deutsch. Chem. Ges.* xvi. 1596.

[5] *Ibid.* xviii. 1400.

Orthodinitrotoluene (1 : 2 : 6) can best be obtained pure by converting *a*-trinitrotoluene into dinitroparatoluidine, and replacing the amido-group of this by hydrogen. It crystallizes in broad, golden needles, melting at 60°—61°.[2]

Symmetric Dinitrotoluene (1 : 3 : 5) may be prepared from the dinitroparatoluidine which melts at 168°, and from the dinitro-orthotoluidine melting at 208°, by suspending these in concentrated nitric acid and saturating the well-cooled liquid with nitrogen trioxide; the product is then brought in small portions at a time into eight or ten parts of absolute alcohol, the solution cooled as soon as the evolution of nitrogen has ceased, and the dinitrotoluene then precipitated with water. On recrystallization from hot water it is obtained in small needles, whilst it crystallizes from petroleum spirit in small prisms, which join to form chain-like masses. It melts at 92° and combines with benzene, forming a double compound, $C_7H_6(NO_2)_2 + C_6H_6$, crystallizing in large prisms which effloresce in the air.[3]

γ-Dinitrotoluene. Beilstein and Kuhlberg obtained this compound by agitating metanitrotoluene with nitric acid of specific gravity 1·54 for a long time. It crystallizes from carbon disulphide in long needles melting at 60°.

TRINITROTOLUENES, $C_6H_2(NO_2)_3CH_3$.

2026 *a-Trinitrotoluene* (1 : 2 : 4 : 6) is formed when toluene[4] or ordinary dinitrotoluene[5] is heated for some days with a mixture of nitric and sulphuric acids. It may be more rapidly prepared by dropping toluene into a mixture of pure nitric acid and sulphuric acid containing a large quantity of sulphur trioxide and warming on the water-bath.[6] It is very slightly soluble in cold, more readily in hot alcohol, from which it crystallizes in large, rhombic tablets or golden needles melting at 82°. On heating with ten times its weight of fuming nitric acid to 180° it is converted into symmetric trinitrobenzene.[1] When aniline is added to its alcoholic solution, the compound $C_7H_5(NO_2)_3 + C_6H_7N$ is obtained in long, red, lustrous needles melting at 83°—84°.[2]

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[1] Claus and Becker, *Ber. Deutsch. Chem. Ges.* xviii. 1336.

[2] Städel and Becker, *Liebig's Ann.* ccxvii. 205; Städel, *ibid.* ccxxv. 384.

[3] Städel, *Ber. Deutsch. Chem. Ges.* xiv. 901; *Liebig's Ann.* ccxvii. 189; Hübner, *ibid.* ccxxii. 74; Neville and Winther, *Ber. Deutsch. Chem. Ges.* xvi. 2985.

[4] Wilbrandt, *Ann. Chem. Pharm.* cxxviii. 178.

[5] Tiemann, *Ber. Deutsch. Chem. Ges.* iii. 217.

[6] H. Schmitt, private communication.

β-Trinitrotoluene. Beilstein and Kuhlberg, by boiling metanitrotoluene with nitric and sulphuric acids, obtained a trinitrotoluene, the purity of which they doubted, adding that the small quantity of substance obtained by them was probably a mixture. Hepp then proved that at least two trinitrotoluenes are formed from metanitrotoluene, and that these can be separated by repeated crystallization from alcohol or carbon disulphide.

β-Trinitrotoluene, which is only formed in small quantity, is readily soluble in carbon disulphide, slightly in cold, more readily in hot alcohol, and freely in ether and acetone. It crystallizes on the gradual evaporation of its solution in the last-named solvent in transparent, asymmetric prisms melting at 112°; whilst it separates from alcohol in dazzling white plates or flat needles. On heating with alcoholic ammonia, a dinitrotoluidine is formed which melts at 94°; it is also readily attacked by aniline and caustic soda solution.

γ-Trinitrotoluene is only very slightly soluble in carbon disulphide and cold alcohol, and separates from hot alcohol in hard, compact, yellowish white crystals, while it crystallizes from acetone in small, hexagonal tablets, melting at 104°.

Concentrated alcoholic ammonia converts it, even in the cold, into a dinitrotoluidine, melting at 192°—193°.

On adding aniline to a hot, alcoholic solution of γ-trinitrotoluene, combination does not occur as in the case of the symmetric trinitrotoluene, but γ-dinitrotolylphenylamine is obtained, diazo-amidobenzene being probably simultaneously formed:

$$CH_3.C_6H_2(NO_2)_3 + 3C_6H_5.NH_2 =$$
$$CH_3.C_6H_2(NO_2)_2N(C_6H_5)H + C_6H_5N_2.NH.C_6H_5 + 2H_2O.$$

This compound forms orange-coloured needles melting at 142°.

γ-Trinitrotoluene is also readily attacked by caustic soda solution, and it must, therefore, like β-trinitrotoluene contain two nitroxyls in adjacent positions (Part III. p. 92).

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[1] Claus and Becker, *Ber. Deutsch. Chem. Ges.* xvi. 1596.
[2] Hepp, *Liebig's Ann.* ccxv. 344.

CHLORONITROTOLUENES, $C_6H_3Cl(NO_2)CH_3$.

2027 *Parachlororthonitrotoluene* (4 : 2) has been prepared from ordinary dinitrotoluene. It is slightly soluble in cold alcohol, readily volatilizes with steam, and crystallizes in needles melting at 38°. It is not attacked by chromic acid solution.[1]

Orthochloroparanitrotoluene (2 : 4). Wachendorff obtained this compound by heating paranitrotoluene with antimony chloride to 100°. It is very readily volatile in steam, dissolves freely in alcohol, and forms long, pointed crystals melting at 64°–65°. Potassium permanganate oxidizes it to chloronitrobenzoic acid.[2] Lellmann has converted it into orthochlorotoluene and orthochlorobenzoic acid.[3]

Wachendorff found that metanitrotoluene could not be chlorinated. Wroblevsky, by the action of nitric acid on crude liquid chlorotoluene, obtained two liquid nitrochlorotoluenes;[4] Engelbrecht, on the other hand, employing crystalline parachlorotoluene, obtained two solid compounds which he was unable to separate completely.[5]

Parachlorometatoluene (4 : 3) has been prepared from metanitroparatoluidine by means of the diazo-reaction, and is identical with one of Wroblevsky's compounds. It is a strongly refractive, golden-yellow liquid, which boils at 260°–261° and solidifies at a low temperature to yellow needles melting at 7°.[6]

BROMONITROTOLUENES, $C_6H_3Br(NO_2).CH_3$.[7]

Br : NO_2		Melting-point.
2 : 5	crystals	76·3°
2 : 4	needles	74°—75°
3 : 2	liquid	—
3 : 5	prisms[8]	86°
5 : 2	rhombic crystals[9]	55°
4 : 2	fine needles[10]	45°·5
4 : 3	crystals	31°—32°

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[1] Beilstein and Kuhlberg, *Ann. Chem. Pharm.* clviii. 336.

[2] *Ibid.* clxxxv. 273.

[3] *Ber. Deutsch. Chem. Ges.* xvii. 534.

[4] *Ann. Chem. Pharm.* clxviii. 203.

[5] *Ber. Deutsch. Chem. Ges.* vii. 797.

[6] Gattermann and Kaiser, *ibid.* xviii. 2599.

[7] Neville and Winther, *ibid.* xiv. 417.

[8] Wroblevsky, *Ann. Chem. Pharm.* cxcii. 203.

[9] Grete, *ibid.* clxxvii. 246.

[10] Beilstein and Kuhlberg, Hübner and Roos, *Ber. Deutsch. Chem. Ges.* vi. 799.

TOLUENEDISULPHONIC ACIDS, $C_6H_3(CH_3)(SO_3H)_2$.

2029 *a-Toluenedisulphonic acid* $(CH_3 : SO_3H : SO_3H = 1 : 2 : 4)$, is a thick liquid which can be heated above 100° without decomposition; it may be prepared by heating toluene, or its ortho- and para-sulphonic acids with fuming sulphuric acid,[1] as well as by passing toluene vapour into concentrated sulphuric acid heated to 240°.[2] Its amide, $C_6H_3(CH_3)(SO_2.NH_2)_2$, is tolerably soluble in warm water, and crystallizes in prisms melting at 185°–186°.

Senhofer and Forber, by heating toluene with a mixture of sulphuric acid and phosphorus pentoxide, obtained a γ-toluenesulphonic acid,[3] which is, according to Claësson, identical with the *a*-acid.[4]

β-Toluenedisulphonic acid is obtained in small quantities in the preparation of the *a*-compound, and is also formed when toluenemetasulphonic acid is treated with fuming sulphuric acid (Hakansson). Its amide melts at 224° (Claësson).

γ-Toluenedisulphonic acid (1 : 3 : 5). When orthotoluidine is heated with fuming sulphuric acid or with chlorosulphonic acid, toluidinedisulphonic acid $(CH_3 : NH_2 : SO_3H : SO_3H = 1 : 2 : 3 : 5)$ is formed; this yields a crystalline diazo-compound, $CH_3.C_6H_2(N_2SO_3)SO_3H$, which is, according to Neville and Winther, converted into the toluenedisulphonic acid by heating with absolute alcohol under pressure,[5] while Limpricht and Hasse observed that ethoxytoluenedisulphonic acid, $CH_3.C_6H_2(OC_2H_5)(SO_3H)_2$ is thus formed. In order to obtain the former, the diazo-compound is converted into iodotoluenedisulphonic acid, and this heated with concentrated hydriodic acid.

γ-Toluenedisulphonic acid forms an amide which crystallizes in small lustrous plates melting above 240°.[6]

TOLUENETRISULPHONIC ACIDS, $C_6H_2(CH_3)(SO_3H)_3$.

Only one of the six toluenetrisulphonic acids which are theoretically possible is known; it is obtained by gradually heating potassium α-toluenedisulphonate with three molecules of chlorosulphonic acid to 240°, until the product forms a clear solution in water. The barium salt is then prepared, and from this the potassium salt, which is converted by the action of phosphorus pentachloride into toluenetrisulphonic chloride, $C_6H_2(CH_3)(SO_2Cl)_3$, which crystallizes from chloroform in rhombic tablets melting at 153°. On heating with water to 130°–140° the free acid is obtained; it crystallizes with six molecules of water in long, fine needles.[1]

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[1] Hakansson, *Ber. Deutsch. Chem. Ges.* v. 1084; Claësson and Bey, *ibid.* xiii. 1170.

[2] Gnehm, *ibid.* x. 542; see also Fahlberg, *ibid.* xii. 1052.

[3] *Ann. Chem. Pharm.* clxiv. 226.

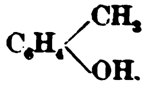
[4] *Ber. Deutsch. Chem. Ges.* xvii. Ref. 284.

[5] *Ibid.* xv. 2998.

[6] *Ibid.* xviii. 2177.

MONOHYDROXYTOLUENES AND ALLIED BODIES.

THE CRESOLS,



$C_6H_4\begin{matrix}\diagup CH_3\\ \diagdown OH.\end{matrix}$

2030 In 1851 Städeler discovered in the urine of the cow, together with phenylic acid, a very similar body which he named *Taurylic acid*, and considered to be the next higher homologue of phenylic acid.[2] As the question was subsequently raised whether the creosote discovered by Reichenbach in wood-tar is identical with phenol or not, Fairlie, under Williamson's directions, conducted an investigation on the so-called coal-tar creosote (Part III. p. 70) and found in it "*hydrate of cresyl*," C_7H_8O, the homologue of phenyl hydrate; he describes this compound as a strongly refractive liquid smelling like phenol and boiling at 203°, and investigated its properties with some care.[3] Duclos discovered the same compound in tar from pine-wood[4] and Marasse in that from beech-wood.[5]

Griess obtained cresol or cresyl alcohol artificially by boiling diazotoluene nitrate with water,[6] and Wurtz by fusing toluenesulphonic acid with caustic potash.[7]

Engelhardt and Latschinow were the first to prove that three isomeric cresols exist; they obtained pure paracresol, or, as they called it, α-cresol, by fusing tolueneparasulphonic acid with caustic potash, and from ordinary toluidine by Griess' reaction. By the same reactions they prepared β-cresol from the orthosulphonic acid and pseudotoluidine (orthotoluidine), but they did not obtain it in a pure state. They further found that thymol, $C_6H_3(CH_3)(C_3H_7)OH$, on heating with phosphorus pentoxide, decomposes into propylene and γ-cresol.[1] This metacresol was then obtained in larger quantities by Oppenheim and Pfaff by heating hydroxyuvitic acid with lime.[2]

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[1] Claësson, *Ber. Deutsch. Chem. Ges.* xiv. 307.

[2] *Ann. Chem. Pharm.* lxxvii. 188.

[3] *Chem. Soc. Journ.* vii. 232.

[4] *Ann. Chem. Pharm.* cix. 135.

[5] *Ibid.* clii. 64.

[6] *Jahresber.* 1866, 458.

[7] *Ann. Chem. Pharm.* cxliv. 121.

Kekulé obtained pure orthocresol by acting with nitrous acid on orthotoluidine and by heating carvacrol (cymophenol), an isomeride of thymol, with phosphorus pentoxide.[3]

The constitution of the three cresols was determined with certainty by Barth, who showed that on fusion with caustic potash, orthocresol is oxidized to salicylic acid, metacresol to hydroxybenzoic acid, and paracresol to parahydroxybenzoic acid (Part III. p. 45).[4]

Further investigations have shown that the cresol contained in coal-tar is a mixture of the three isomerides.[5] It is obtained from the oily mother-liquor left after crystallization of the phenol by dissolving in caustic soda, removing all naphthalene by a current of steam, and then fractionally precipitating the solution with hydrochloric acid; the cresol separates out first, the phenol, being a stronger acid, remaining in solution.[6] According to another method, the solution is neutralized with hydrochloric acid and the mixture agitated with sufficient baryta water to dissolve all the phenol.[7] The cresol obtained is purified by distillation until it boils at 198°–203°. Derivatives of all three cresols can be prepared from it, but only the para-compound can actually be extracted in the pure condition. This is effected by treating the mixture with benzoyl chloride, paracresyl benzoate, melting at 78°, being formed; this is separated by pressing from the liquid ethers of the two other cresols; purified by re-crystallization, and decomposed by caustic soda (Engelhardt and Latschinow). Baumann has pointed out that the cresol (taurylic acid) contained in the urine of graminivora occurs as the potassium salt of paracresylsulphuric acid.[8] This compound also occurs in human urine during scarlatina, erysipelas, &c.[9] The urine of horses also contains some orthocresyl

[1] *Zeitschr. Chem.* 1869, 618.
[2] *Ber. Deutsch. Chem. Ges.* viii. 884.
[3] *Ibid.* vii. 1006.
[4] *Ann. Chem. Pharm.* cliv. 356.
[5] Schotten and Tiemann, *ibid.* xi. 783.
[6] Müller, *Zeitschr. Chem.* 1865, 271.
[7] Ihle, *Journ. Prakt. Chem.* [2] xiv. 442.
[8] *Ber. Deutsch. Chem. Ges.* ix. 1389, 1716.
[9] Brieger, Hoppe-Seyler's *Zeitschr.* iv. 204.

sulphuric acid.[1] Para- and ortho-cresol are also formed when the liver of the horse is caused to putrefy with the addition of river-mud.[2]

2031 *Orthocresol* is best obtained by adding 12 parts of pure potassium nitrite to a solution of 15 parts of orthotoluidine and 15 parts of sulphuric acid in 500 parts of water; the liquid is heated by a current of steam, and the cresol distilled off in the steam.[3] It forms colourless crystals, melts at 30° and boils at 188°. Its aqueous solution is coloured blue by ferric chloride; on fusion with caustic potash it is oxidized to salicylic acid. When administered to a dog it appears in the urine as orthocresylsulphuric acid and oxycresylsulphuric acid (hydrotoluquinonesulphuric acid). By the action of potassium chlorate and hydrochloric acid it yields di- and tri-chlorotoluquinone.[4]

Orthocresyl oxide, $(CH_3.C_6H_4)_2O$. If a few grains of iodine and then some aluminium are added to boiling orthocresol, aluminium orthocresylate, $(CH_3.C_6H_4O)_6Al_2$, is formed, and this solidifies on cooling to a black vitreous mass. When subjected to dry distillation it yields, among other products, orthocresol and orthocresyl oxide, which is a colourless liquid smelling like the geranium, and boiling at 272°–278°.[5]

Dichlororthocresol, $C_6H_2Cl_2(CH_3).OH$, is obtained by the action of chlorine on boiling orthocresol; it crystallizes from alcohol in needles with a silky lustre, melts at 55° and on oxidation undergoes partial combustion, at the same time yielding trichlorotoluquinone.[6]

Bromorthocresol, $C_6H_3Br(CH_3)OH$, has been prepared from bromorthotoluidine, and crystallizes from alcohol in lustrous golden needles melting at 88·5°.[7]

a-Nitro-orthocresol, $C_6H_3(CH_3)(NO_2)\,OH\,(1:3:2)$, is formed when a solution of 2 parts of orthocresol in 2 parts of glacial acetic acid is allowed to drop into a cold mixture of 3 parts of nitric acid, of specific gravity 1·4, and 6 parts of glacial acetic acid. It is insoluble in water and crystallizes from dilute alcohol in long, yellow prisms melting at 69·5°. Its potassium salt crystallizes in garnet-red, rhombic tablets.

When the hydrochloride of the amidocresol obtained from this compound is distilled with sodium formate, a methenyl compound is formed; this reaction is characteristic of all the amidophenols in which the amido-group is in the ortho-relation to the hydroxyl.[1]

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[1] Preusse, *ibid.* ii. 355; *Ber. Deutsch. Chem. Ges.* xi. 1911.

[2] Baumann and Brieger, Hoppe-Seyler's *Zeitschr.* iii. 149, 252.

[3] Schotten and Tiemann, *loc. cit.*

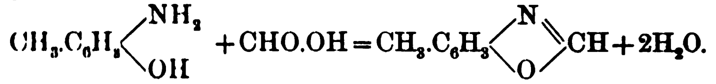
[4] Southworth, *Ann. Chem. Pharm.* clxviii. 273.

[5] Gladstone and Tribe, *Journ. Chem. Soc.* 1886, i. 25.

[6] Claus and Riemann, *Ber. Deutsch. Chem. Ges.* xvi. 1598.

[7] Wroblevsky, *Ann. Chem. Pharm.* clxviii. 165.

Methenylamidorthocresol is formed according to the following equation:



$$CH_3.C_6H_3\left\langle\begin{matrix}NH_2\\OH\end{matrix}\right. + CHO.OH = CH_3.C_6H_3\left\langle\begin{matrix}N\\O\end{matrix}\right\rangle CH + 2H_2O.$$

It is a crystalline mass which melts at 38°—39°, boils at 200° and has a peculiar smell, resembling that of acetamide, characteristic of these anhydro-bases.

A liquid nitrocresol boiling at 226°—230° is formed together with the solid compound.[2]

β-Nitro-orthocresol (1 : 5 : 2) is prepared from the corresponding nitro-orthotoluidine by means of the diazo-reaction or by heating it with strong caustic soda. It crystallizes in fine, light yellow needles and melts at 95°.[3] On reduction it yields *β-amido-orthocresol*, the hydrochloride of which crystallizes readily.

γ-Nitro-orthocresol (1 : 4 : 2) is formed together with the *α*-compound when orthocresol is nitrated at as low a temperature as possible. On distillation with steam it remains behind. It is only very slightly soluble in water, readily in alcohol and benzene, and crystallizes in white needles united to form bushy aggregates, or in small, hexagonal tablets, being, therefore, dimorphous like paranitrophenol. It melts at 82°—85°, and forms a potassium salt, crystallizing in small brass-yellow plates. On reduction it is converted into *γ-amido-orthophenol*, crystallizing in tablets which have a silvery lustre and melt at 175°. When oxidized in an acid solution, it is converted into toluquinone. Hirsch has been unable to obtain the liquid nitrocresol mentioned above.[4]

Dinitro-orthocresol, $C_6H_2(CH_3)(NO_2)_2OH$ (1 : 3 : 5 : 2), was first obtained from orthotoluidine, nitro-orthotoluidine ($NH_2 : NO_2 = 2 : 5$), and orthotoluidinesulphonic acid ($NH_2 : SO_3H = 2 : 3$), by converting them into diazo-compounds and heating these with dilute nitric acid.[5] It is also formed by the further nitration of α- and γ-nitro-orthocresol (Hirsch), and of orthocresyl ether.[1] It crystallizes from alcohol in long, yellow prisms, and from petroleum-spirit in broad, golden-yellow needles, which have a blue surface-lustre and melt at 86°.

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[1] Ladenburg, *Ber. Deutsch. Chem. Ges.* ix. 1524; x. 1124.
[2] Hofmann and Miller, *ibid.* xiv. 467.
[3] Neville and Winther, *ibid.* xv. 2978.
[4] Hirsch, *ibid.* xviii. 1511.
[5] Neville and Winther, *ibid.* xiii. 1496; Nölting, and Salis, *ibid.* xiv. 987.

On the reduction of its ethyl ether the diamido-ether is obtained, and this compound forms a chrysoidine with diazobenzene (Part III. p. 301), thus affording a further proof that the nitroxyl groups in dinitrocresol have the meta-relation to each other.

2032 *Metacresol.* In order to prepare this compound, 100 grammes of thymol are heated for ten or twelve hours with 35 grammes of phosphorus pentoxide, the propylene which is evolved being passed into bromine in order to obtain its bromide as a by-product. The syrupy mass is brought into 115—120 grammes of fused caustic potash, and the mixture kept in a state of fusion and well agitated for five or ten minutes. It is then dissolved in water and extracted with ether in order to remove cresyl phosphate and other substances; the residue is then decomposed with hydrochloric acid, the metacresol taken up with ether, the latter distilled off, and the product purified by distillation in a current of carbon dioxide (Schotten and Tiemann).

It is a liquid which smells like phenol, boils at 201° and does not solidify in a freezing mixture; if, however, a crystal of phenol be thrown into the cooled liquid it solidifies immediately, forming crystals resembling those of phenol and melting at 3°—4°.[2] Its aqueous solution is coloured violet to blue by ferric chloride; by the action of potassium chlorate and hydrochloric acid, it is converted into dichlorotoluquinone (Southworth).

Metacresyl oxide, $(CH_3.C_6H_4)_2O$, is formed, together with propylene and other products by the dry distillation of aluminium thymol, $(C_3H_7(CH_3)C_6H_3O)_6Al_2$, and is a liquid boiling at 284°—288°.[3]

Bromometacresol, $C_6H_2Br(CH_3)OH$ (1 : 3 : 5), has been prepared from the corresponding bromotoluidine, and crystallizes from hot water in white needles melting at 56°—57°.[4]

Nitrometacresol, $C_6H_3(CH_3)(NO_2)OH$ (1 : 3 : 5), is prepared from symmetric dinitrotoluene; it crystallizes from hot water in light yellow, lustrous prisms, containing one molecule of water of crystallization. It is deposited from solution in benzene in anhydrous crystals melting at 90°—91°. On reduction it yields amidometacresol, the hydrochloride of which is readily soluble.[1]

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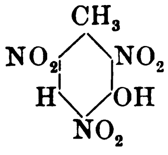
[1] Städel, *Ann. Chem. Pharm.* ccxvii. 158.
[2] Städel, *Ber. Deutsch. Chem. Ges.* xviii. 3443.
[3] Gladstone and Tribe, *Journ. Chem. Soc.* 1882, i. 5.
[4] Neville and Winther, *Ber. Deutsch. Chem. Ges.* xv. 2991.

Trinitrometacresol, $C_6H(NO_2)_3(CH_3)OH$ ($NO_2 : NO_2 : NO_2 = 2 : 4 : 6$), was obtained by Duclos from crude cresol; Nölting and Salis have prepared it from metacresol, which is readily converted into the trinitro-compound, while its isomerides yield the dinitrocresols as final products. In order to prepare it, coal-tar cresol is dissolved in 3 parts of concentrated sulphuric acid, and allowed to stand in a warm place until cresol no longer separates out on the addition of water. Crude nitric acid is then gradually added to the aqueous solution, which is subsequently evaporated, the residue being extracted with a little water to remove picric and oxalic acids, and repeatedly re-crystallized from alcohol.[2]

Liebermann and van Dorp obtained it by heating nitrococcussic acid,[3] $C_6(NO_2)_3(CH_3)(CO_2H)OH$, and Emmerling and Oppenheim by the action of nitric acid on hydroxyuvitic acid, $C_6H_2(CH_3)(CO_2H)\,OH$.[4] Trinitrometacresol is slightly soluble in cold, somewhat more readily in hot water, and crystallizes in long, yellow needles melting at 105°—106°.

When its ethyl ether is heated with alcoholic ammonia, no nitrous acid is removed (Nölting and Salis), which proves that it contains no nitroxyl groups in the ortho-relation (Part III. p. 63), and, therefore, that trinitrometacresol has the following constitution:



2033 *Paracresol* is most readily obtained from paratoluidine, as orthocresol is from orthotoluidine; it crystallizes in prisms melting at 36°, and boils at 198°; its aqueous solution is coloured blue by ferric chloride. It differs from its isomerides in not yielding a chlorinated toluquinone by the action of potassium chlorate and hydrochloric acid.

Paracresyl oxide $(CH_3.C_6H_4)_2O$, has been prepared by Gladstone and Tribe in the same manner as the ortho-compound, and is also formed by heating paracresol to 300° with zinc chloride. It crystallizes from alcohol in small lustrous plates, and from petroleum spirit in needles which have a silky lustre, and melt at 165°, but readily volatilize at 100°.[1]

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[1] *Ber. Deutsch. Chem. Ges.* xv. 2978.
[2] Beilstein and Kellner, *Ann. Chem. Pharm.* cxxviii. 165.
[3] *Ibid.* clxiii. 101.
[4] *Ber. Deutsch. Chem. Ges.* ix. 1094.

Chloroparacresol, $C_6H_3(CH_3)Cl(OH)$ (1 : 3 : 4), is formed by the action of dry chlorine on anhydrous sodium paracresate. It is a colourless liquid which boils at 195°—196°, and has a peculiar, unpleasant, persistent odour. Phosphorus pentachloride converts it into a dichlorotoluene, which yields on oxidation the orthodichlorobenzoic acid melting at 200°.[2]

Dichloroparacresol, $C_6H_2(CH_3)Cl_2.OH$, is formed by the action of chlorine on boiling paracresol; it crystallizes from alcohol in monoclinic needles, and from a hot, concentrated solution in petroleum-ether in long needles melting at 39°; on the gradual evaporation of a dilute solution, it is obtained in transparent prisms with a melting point of 42°; these, however, soon fall to pieces, and the product then melts at 39°. On oxidation the dichlorobenzoic acid melting at 156° is formed (Claus and Riemann).

Bromoparacresol, $C_6H_3(CH_3)Br(OH)$ (1 : 3 : 4), is obtained by the action of bromine on potassium paracresate. It is a liquid which does not solidify in a freezing mixture, boils at 213°—214°, and has a less unpleasant smell than the chlorine compound (Schall and Dralle).

Bromoparacresol (1 : 2 : 4) may be readily obtained by the action of bromine on a solution of paracresol in chloroform; it crystallizes in needles, melting at 17°—18°, and boils at 218°—220°. On fusion with caustic potash it is converted into lutorcinol, $C_6H_3(CH_3)(OH)_2$.[3]

Dibromoparacresol, $C_6H_2(CH_3)Br_2(OH)$, is also formed when potassium paracresate is treated with bromine. It crystallizes from alcohol in prisms which are isomorphous with dichloroparacresol and melt at 49° (Schall and Dralle).

Iodoparacresol, $C_6H_3(CH_3)I(OH)$ (1 : 3 : 4), is an oily liquid, and is obtained by the action of iodine on potassium paracresate; on fusion with potash it yields protocatechuic acid, $C_6H_3(OH)_2CO_2H$, and catechol.

Di-iodoparacresol, $C_6H_2(CH_3)I_2(OH)$, is formed in the preparation of the mono-compound, and crystallizes in small tablets melting at 61·5° (Schall and Dralle).

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[1] Buch, *Ber. Deutsch. Chem. Ges.* xvii. 2638.

[2] Schall and Dralle, *ibid.* xvii. 2528.

[3] Vogt and Henninger, *ibid.* xv. 1081.

α-Nitroparacresol, $C_6H_3(CH_3)(NO_2)OH$ (1 : 3 : 4), is obtained by boiling nitracetparatoluide with caustic soda,[1] and by the nitration of paracresol.[2] It is slightly soluble in water, readily in alcohol, and crystallizes in flat, yellow needles, which melt at 33·5°, and are volatile in steam.

α-Amidoparacresol, $C_6H_3(CH_3)(NH_2)OH$ (1 : 3 : 4) is formed by the reduction of the nitro-compound with tin and hydrochloric acid; it crystallizes from ether in monoclinic prisms, and when heated with formic acid yields *methenylamidoparacresol*, melting at 45° (Hofmann and Miller).

β-Nitroparacresol, $(CH_3 : NO_2 : OH = 1 : 2 : 4)$, is prepared from ordinary dinitrotoluene by reducing it with ammonium sulphide to nitrotoluidine and then replacing the amido-group by hydroxyl. It forms long yellow crystals which melt at 78° and are readily soluble in hot water and alcohol.[3]

β-Amidoparacresol, $(CH_3 : NH_2 : OH = 1 : 2 : 4)$, is obtained by the reduction of the preceding compound, and crystallizes from hot water in small plates melting at 143°—144°.[4]

γ-Amidoparacresol, $(CH_3 : NH_2 : OH = 1 : 4 : 2)$. The hydrochloride of this base is obtained by converting the monacetyl compound of the corresponding diamidotoluene into acetamidocresol, $C_6H_3(CH_3)OH(NH.C_2H_3O)$ and boiling this with hydrochloric acid. It crystallizes in small glistening plates, and on treatment with potassium bicarbonate yields the free base, which forms small lustrous plates or needles, melting at 159°—161° (Wallach).

The constitution of the substituted paracresols follows from their conversion into dihydroxytoluenes.

Dinitroparacresol, $C_6H_2(CH_3)(NO_2)_2OH$(1 : 3 : 5 : 4), has been prepared from the corresponding dinitrotoluidine and by the nitration of cresolsulphonic acid.[5] It is also obtained by warming the diazo-compound prepared from paratoluidinesulphonic acid with nitric acid (Neville and Winther), and by the nitration of paracresol ethyl ether; it crystallizes from dilute alcohol in yellow needles melting at 85°. On the reduction of its ethyl compound, diamidoparacresyl ether, $C_6H_2(CH_3)(NH_2)_2OC_2H_5$, is obtained; this compound forms a chrysoïdine with diazobenzene chloride, proving that the nitroxyls of the dinitrocresol are in the meta-relation to each other.

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[1] Wagner, *Ber. Deutsch. Chem. Ges.* vii. 537; Neville and Winther, *ibid.* xv. 2893.

[2] Armstrong and Thorpe, *Jahresb. Chem.* 1876, 452; Hofmann and Miller, *loc. cit.*

[3] Knecht, *Ann. Chem. Pharm.* ccxv. 83; *Ber. Deutsch. Chem. Ges.* xv. 298. Neville and Winther, *ibid.* xv. 2980.

[4] Wallach, *ibid.* xv. 2831.

[5] Armstrong and Field, *Ber. Deutsch. Chem. Ges.* vi. 974.

Potassium dinitroparaeresate, $C_6H_2(CH_3)(NO_2)_2OK$, crystallizes in red needles and forms the "golden yellow," which was exhibited as a new dye in the Belgian section of the Vienna Exhibition in 1873.[1]

It is also, together with the potassium salt of dinitro-orthocresol, contained in "safronsurrogate," which is used for colouring milk, butter, and cheese.[2]

Victoria yellow or *aniline orange*, which formerly came into the market as a red powder, is the salt of a third dinitrocresol, the constitution of which is unknown. It crystallizes from hot water in yellowish needles, melting at 109°—110°.[3]

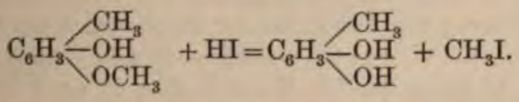
Thiocresols, $C_6H_4(CH_3)SH$, are obtained by the reduction of the corresponding sulphonic chlorides.

		Melting-point.	Boiling-point.
Orthothiocresol[4]	small, delicate plates .	15°	188°
Metathiocresol[5]	liquid	—	188°
Parathiocresol[6]	large plates	43°	189°

DIHYDROXYTOLUENES AND ALLIED BODIES.

HOMOCATECHOL, OR HOMOPYROCATECHIN, $C_6H_3(CH_3)(OH)_2$ (1 : 3 : 4).

2034 Hugo Müller obtained this compound by heating its monomethyl ether, creosol, with hydriodic acid:[7]



$$C_6H_3\begin{cases}CH_3\\OH\\OCH_3\end{cases} + HI = C_6H_3\begin{cases}CH_3\\OH\\OH\end{cases} + CH_3I.$$

It is also formed by fusing creosol with caustic potash,[8] by boiling the diazo-compound of a-amidocresol with water (Neville and Winther), and by submitting *a*-homoprotocatechuic acid, $C_6H_2(CH_3)(OH)_2CO_2H$, to dry distillation.[1]

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[1] Piccard, *Ber. Deutsch. Chem. Ges.* viii. 685.

[2] Wichelhaus, *ibid.* vii. 770.

[3] Martius and Wichelhaus, *ibid.* ii. 206.

[4] Hübner and Post, *Ann. Chem. Pharm.* clxix. 30.

[5] *Ibid.*

[6] Märcker, *ibid.* cxxxvi. 79.

[7] *Chem. News*, x. 269.

[8] Tiemann and Koppe, *Ber. Deutsch. Chem. Ges.* xiv. 2025.

Homocatechol is a syrup which readily dissolves in water, alcohol, ether, and benzene, and can be distilled without decomposition. It reduces silver salts and Fehling's solution in the cold, and gives a green colouration with ferric chloride, which is converted into a reddish violet by the addition of a little ammonia or carbonate of soda.

Homocatechol monomethyl ether or *Creosol*, $C_6H_3(CH_3)(OCH_3)OH(1:3:4)$, occurs in beechwood-tar-creosote and in the products of distillation of guaiacum resin.[2] In order to prepare it, the portion of creosote boiling at about 220° is dissolved in ether and treated with very concentrated alcoholic potash; potassium creosate, $C_8H_9KO_2 + 2H_2O$, separates out in needles and is then decomposed by dilute sulphuric acid. It may also be prepared by heating *a*-homovanillic acid, $C_6H_3(OH)(OCH_3)CH_2.CO_2H$, with lime (Tiemann and Nagai). It is a strongly refractive liquid boiling at 220°, and possesses a feeble odour which resembles that of vanilla and is very pleasant when the vapour is dilute. It produces a metallic mirror when warmed with a solution of a silver salt, and its alcoholic solution is coloured emerald-green by ferric chloride. Phosphorus chloride converts it into parachlorometacresol methyl ether, $C_6H_3Cl(CH_3)OCH_3$, $(CH_3:OCH_3:Cl=1:3:4)$, a liquid boiling at 185°.[3]

Homocatechol dimethyl ether, $C_6H_3(CH_3)(OCH_3)_2$, also occurs in creosote, and is obtained pure by boiling potassium creosate with methyl iodide and wood-spirit. It is a liquid which boils at 214°—215° and possesses the characteristic smell of the indifferent oils which are obtained from crude wood-tar. It is insoluble in water and alkalis, and is not coloured by ferric chloride.[4]

2035 *Creosote* was discovered by Reichenbach in the year 1832, both in the tar and the pyroligneous acid obtained by the distillation of beech-wood.[5] He describes it as a colourless, strongly refractive liquid, which begins to boil at 203° and possesses an unpleasant penetrating odour, at the same time resembling that of smoked meat, and a burning taste. He investigated its properties very carefully, and found that it coagulates albumin, and that fresh meat which has been soaked in creosote for half an hour to an hour can be dried without undergoing putrefaction. Such meat is very tasty, and Reichenbach therefore concluded that creosote is the antiseptic principle contained in smoke. He derived its name from this power of preserving meat, its most peculiar and most striking property, one too which had been known from the earliest times; he remarks, "The Greek word *κρέας*, meat, has a genitive *κρέατος*, or *κρέαως*, contracted to *κρέως*; *σώζω* signifies to preserve, or save; the two may be etymologically united in the word creosote, which expresses meat-preserving or decay-saving."

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[1] Tiemann and Nagai, *Ber. Deutsch. Chem. Ges.* x. 210.

[2] Hlasiwetz, *Ann. Chem. Pharm.* cvi. 339.

[3] Biechele, *ibid.* cli. 115.

[4] Tiemann and Mendelsohn, *Ber. Deutsch. Chem. Ges.* viii. 1136.

[5] Schweiger's *N. Jahrb. Chem. Phys.* vi. 301, 345; vii. 1, 57; viii. 57, 399.

Very soon after this, Runge discovered carbolic acid, and Laurent phenyl hydrate, in coal-tar, the identity of these bodies being recognised somewhat later. No clear views, however, were held as to the relation existing between phenol and creosote, and a confusion arose which was maintained for many years with an obstinacy unparalleled in the annals of our science.

Runge and Laurent showed that creosote, in spite of many similarities, is quite a different substance from the compound obtained by them. Phenol differs from creosote more especially in being an acid, in possessing a different boiling-point, in crystallizing when cooled, and in its different behaviour towards chlorine, bromine, and nitric acid. Runge moreover adds that it imparts to meat preserved by it an abominable taste.

Reichenbach, nevertheless, considered carbolic acid to be identical with his creosote, the more so as he thought that he had also discovered it in coal-tar and bone-oil.

Gmelin was also of this opinion; according to him, carbolic acid, phenyl hydrate, and creosote, are chemically identical, differing only in degree of purity. Gmelin's views found universal acceptance; crystallized carbolic acid soon came into the market under the name of creosote and displaced the genuine substance obtained from wood-tar.

Gorup-Besanez, who had some of the latter body, which had been prepared by Reichenbach at Blansko, in Moravia, at his disposal, compared it with "crystallized creosote," and, like Runge and Laurent, found them to be completely different; the amount of substance in his possession, however, did not admit of a close investigation.

Some years later, Batka supplied him with fresh samples of creosote from Blansko, and he found that when acted upon by nitric acid, no picric acid was formed, while potassium chlorate and hydrochloric acid instead of giving chloranil $C_6Cl_4O_2$, gave a similar substance, which, however, contained hydrogen.[1]

These results, however, attracted but little attention; Gmelin, indeed, mentions them in his hand-book but only to add that Gorup-Besanez, to prove that creosote is a distinct substance, ought to have prepared it himself instead of investigating a commercial product.

Two years later, Gorup-Besanez published a more extended treatise on creosote; his determination of its composition agreed with that of Ettling, who had analysed a specimen sent by Reichenbach to Liebig.

By the action of chlorine he obtained pentachloroxylone, $C_{13}H_7Cl_5O_2$, and hexchloroxylone, $C_{13}H_6Cl_6O_2$, substances which were very similar to the chlorinated quinones obtained by Städeler.[2]

About the same period Völkel published a paper on the distillation products of wood, in which he relates his investigation of the creosote obtained from the tar in a pyroligneous acid works at Solothurn. He purified it by repeated solution in caustic potash, precipitation with sulphuric acid and distillation. The liquid, after purification in this manner, boiled at 202°—208°, and in its general properties resembled Reichenbach's compound, but had a different composition, as the following results of the analyses conducted by Ettling, Gorup-Besanez, and Völkel show:[3]

	Creosote from Blansko. (Mean of 8 Analyses.)	Creosote from Solothurn. (Mean of 3 Analyses.)
Carbon	75·21	72·45
Hydrogen	7·90	7·10
Oxygen	16·89	20·45
	100·00	100·00

Deville had previously analysed creosote prepared by Pelletier, and obtained numbers only differing slightly from those of Völkel.

Völkel considered that Gorup-Besanez had not purified his creosote sufficiently, whereupon the latter treated it repeatedly by Völkel's method, without, however, altering the results obtained by analysis to any appreciable extent.[4]

In the same year, Williamson published the results of an investigation made by Fairlie towards the solution of the question whether coal-tar creosote consists chiefly of carbolic acid; he thus discovered the homologue of phenol, cresyl hydrate or cresol, which boils at 203°, or at nearly the same temperature as creosote, thus introducing a new source of confusion. The research had no direct bearing on the real issue.

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[1] *Ann. Chem. Pharm.* lxxviii. 231.

[2] *Ibid.* lxxxvi. 233.

[3] *Ibid.* lxxxvi. 66, 93.

[4] *Ibid.* xcvi. 39.

A new chapter in the history of creosote begins with Hlasiwetz's investigation "On Beech-Wood Tar Creosote and the Products of Distillation of the Guaiacum Resin." He had already obtained the compound $C_8H_{10}O_2$ from the creosote from Blansko, and now found it in the distillation products of guaiacum resin, together with its lower homologue, guaiacol, $C_7H_8O_2$, which Deville and Pelletier had already obtained from the same source; he therefore called his compound creosote-guaiacol or creosol.

Hlasiwetz concluded that creosote is a kind of ether of the latter, and probably contains the radical C_9H_{11}, thus simply explaining the fact that it contains more carbon than creosol.

In the following year Duclos published a paper on cresyl alcohol, which he had not only found in coal-tar, but also in the tar from the gas-works at Giessen where only wood, and for the most part fir-wood, was used.[1]

In criticism of this paper, Gorup-Besanez observed that these results were in opposition to all the facts known concerning the distillation products of wood, in which no phenols had yet been found. If Duclos' results were to be accepted, it would be necessary to assume that fir-wood yields different products from beech-wood.

In the meantime Gerhardt calculated the formulæ of the chlorinated xylones as $C_8H_5Cl_3O_2$ and $C_8H_4Cl_4O_2$, according to which they appear to be homologues of the chloroquinones, thus confirming Hlasiwetz's results; Gorup-Besanez then undertook the reïnvestigation of these compounds, but could not obtain any creosote from Blansko; this source had failed.

In the year 1864, Hugo Müller made an important addition to the history of creosote; he investigated a sample which had been prepared in London from Stockholm-tar and appeared to be identical with that from Blansko. By treating it with hydriodic acid be obtained methyl iodide and homocatechol (p. 31).

These different researches afforded a complete proof that wood-tar creosote has nothing in common with coal-tar creosote.

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[1] *Ann. Chem. Pharm.* cix. 135.

The only obstacles now remaining to a complete concordance of opinion on the subject were Reichenbach's statement, which he had never confirmed, that his creosote is contained in coal-tar, and that of Duclos that wood-tar contains phenols, which no one else had been able to detect.

2036 The creosote question seemed to have received a final answer, but it was nevertheless not yet settled. In the year 1865, A. E. Hofmann investigated several commercial products which he obtained from various firms as genuine beech-wood-tar creosote, and found that they consisted chiefly of phenol. Being unacquainted with the researches of Hlasiwetz and Müller, he called the existence of creosote in question and concluded that it was nothing but impure phenyl hydrate, the chlorinated xylones being mixtures of chloranil with chlorinated phenols. The name of creosote ought, therefore, to be removed from our list of chemical compounds, though this would not prevent its use as a commercial term.

Gorup-Besanez replied to this by pointing out that Hofmann had only proved a fact which had long been known, that phenylic acid was often sold under the name of creosote. It was impossible that the firms mentioned by him could have sent him genuine creosote, because this article had long disappeared from the German market.[1]

This incident had a fortunate conclusion both for Gorup-Besanez and for the facts. Fresenius corrected his statement, pointing out that the "Verein für chemische Industrie" at Mayence worked up beech-wood-tar for creosote. The investigation of this showed that it differed from the Blansko samples, but was probably identical with those from Solothurn. Gorup-Besanez succeeded in extracting from it a considerable quantity of guaiacol together with a smaller amount of creosol; by the action of potassium chlorate and hydrochloric acid on the crude creosote he obtained tetrachloroguaiacone, $C_7H_2Cl_4O_2$, and tetrachlorocreosone, $C_8H_4Cl_4O_2$, homologues of chloranil. When he treated creosote with hydriodic acid, he obtained methyl iodide and catechol, which were undoubtedly derived from the guaiacol. He assumed that catechol is the lower homologue of guaiacol and creosol, both of which yield chlorine products homologous with chloranil.

He concluded from his analysis that Rhenish creosote contains the radical C_3H_5.[2]

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[1] *Journ. Prakt. Chem.* xcvii. 63.

[2] *Ann. Chem. Pharm.* cxliii. 129.

Marasse opposed this view; Gorup-Besanez had thought that the fraction boiling between 199° and 208° is the allyl ether of guaiacol, the latter being derived from it by the action of caustic potash. If this were the case, allyl alcohol or some similar compound must be simultaneously formed, whereas no one had hitherto observed this. Guaiacol, he continues, may be the methyl ether and not the homologue, of catechol, bearing the same relation to it as creosol to homocatechol. The difference between the composition of creosote and that of the two methyl ethers contained in it is easily accounted for on the supposition that it contains substances which boil at the same temperature as guaiacol and creosol but are richer in carbon and poorer in hydrogen.

He also found that creosote contains, besides ordinary phenol, its homologues cresol and phlorol, which yield the chlorine products now known as tetrachlorotoluquinone and tetrachloroxyloquinone.[1]

The composition of creosote is very variable. Bräuniger found in one sample only traces of phenol and less than 2 per cent. of cresol, and in that investigated by Gorup-Besanez only a little cresol and still less phlorol,[2] while Tiemann and Mendelsohn found large quantities of the latter.[3] The relative amounts of guaiacol and creosol are also subject to great variations; thus Biechle found scarcely any creosol in a second sample of Rhenish creosote obtained by Gorup-Besanez.[4]

The higher boiling fractions contain, moreover, the dimethyl ethers of homocatechol, pyrogallol, dimethylpyrogallol, and propylpyrogallol, which have already been partially described.

The presence of phenols in wood-tar-creosote shows that it is more closely related to the so-called coal-tar creosote than was previously supposed. The latter differs from the former by the absence of guaiacol, creosol, and the dimethyl ethers just mentioned. These must be derived from the characteristic aromatic compounds which various chemists have discovered in wood (Vol. III. Pt. II. p. 583).

ORCINOL, $C_6H_3(CH_3)(OH)_2$ (1 : 3 : 5).

2037 Robiquet discovered this compound in 1829 in *Variolaria dealbata*, and named it orcin, because this lichen had formerly been called *Lichen orcina*, and because the name serves as a reminder that the lichen is used for the preparation of archil (*orseille*).[1]

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[1] *Ann. Chem. Pharm.* clii. 59

[2] *Ibid.* clxxxv. 339.

[3] *Ber. Deutsch. Chem. Ges.* x. 59.

[4] *Ann. Chem. Pharm.* cli. 104.

Orcinol was then further investigated by various other chemists,[2] from whose analyses Gerhardt first calculated its correct formula,[3] his result being confirmed by the researches of Stenhouse.[4]

Orcinol occurs in the free state in all the lichens, the various species of *Rocella*, *Lecanora* and *Variolaria*, which are employed for the preparation of archil and litmus, and is a decomposition product of various acids and ether-like bodies prepared from these lichens. When these compounds are heated with an alkali or submitted to dry distillation, orcinol is formed, *e.g*:

$$\overset{\text{Erythrin.}}{\left.\begin{array}{l} C_7H_5(OH)_2CO_2 \\ C_7H_5(OH)_2CO_2 \end{array}\right\rangle C_4H_6(OH)_2} + 2H_2O = \overset{\text{Orsellinic Acid.}}{2C_7H_5(OH)_2CO_2H} + \overset{\text{Erythrol.}}{C_4H_6(OH)_4}.$$

$$\overset{\text{Lecanoric Acid.}}{\begin{array}{l} C_7H_5(OH)O.CO_2H \\ \qquad\qquad\quad\vert \\ C_7H_5(OH)_2CO \end{array}} + H_2O = \overset{\text{Orsellinic Acid.}}{2C_7H_5(OH)_2CO_2H}.$$

$$\overset{\text{Orsellinic Acid.}}{C_7H_5(OH)_2CO_2H} = \overset{\text{Orcinol.}}{C_7H_6(OH)_2} + CO_2.$$

In order to prepare orcinol, 6 parts of *Rocella fuciformis* are macerated for twenty minutes with 60 parts of milk of lime containing 1 part of lime, the mass filtered and the erythrin precipitated from the filtrate by hydrochloric acid; this is boiled for half an hour with a slight excess of milk of lime, the solution filtered, treated with carbon dioxide to remove the excess of lime, and evaporated nearly to dryness. The orcinol is extracted from the residue by benzene, while erythrol is left behind. When the benzene solution is shaken with water, the orcinol is taken up by the latter and is obtained pure on evaporation.[5] The crude orcinol can also be purified by distillation,[1] which is best carried on *in vacuo*.[2]

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[1] *Ann. Chim. Phys.* xlii. 236.

[2] Dumas, *Ann. Chem. Pharm.* xxvii. 140; Liebig and Will, *ibid.* xxvii. 147; Schunk, *ibid.* xli. 159; liv. 269.

[3] *Compt. Rend. Chim.* 1845, 287.

[4] *Phil. Trans.* 1848, 63; 1849, 393.

[5] Stenhouse.

Vogt and Henninger first prepared orcinol from toluene, by chlorinating toluene in presence of iodine, and warming the chlorotoluene with two to three times its weight of sulphuric acid on the water-bath; two sulphonic acids are thus formed, which readily admit of separation, the barium salt of the one being much more soluble than that of the other, which yields orcinol when fused with caustic potash.[3]

The chlorotoluene obtained by the method described is a mixture of parachlorotoluene with a little orthochlorotoluene; since, however, the side chains of orcinol are arranged symmetrically, an inter-molecular change must take place during its preparation just as in that of resorcinol from benzeneparadisulphonic acid.

Neville and Winther obtained orcinol by fusing symmetric bromotoluenesulphonic acid, the toluenemetadisulphonic acid obtained from orthotoluidinedisulphonic acid, or bromometacresol with caustic potash; they also prepared it by heating metadibromotoluene to 280°—300° with caustic potash and a little water, and finally by replacing the amido-group of amidometacresol by hydroxyl.[4]

Orcinol is also formed, together with parahydroxybenzoic acid, when aloes are fused with caustic soda.[5]

Properties.—Orcinol is readily soluble in water, alcohol, and ether, and crystallizes with one molecule of water in six-sided monoclinic prisms, which effloresce gradually over sulphuric acid, and more rapidly when heated to 100°. It is almost completely precipitated in fine needles when its concentrated solution is warmed with a saturated solution of common salt (Lamparter); it reduces ammoniacal silver solution, has an intensely sweet but unpleasant taste, and melts in the anhydrous state at 106·5°—108° (Neville and Winther). When rapidly heated, it distils almost without decomposition between 287° and 290° (Dumas). Ferric chloride produces a violet-black colouration, and bleaching powder a dark red, soon changing to yellow. In the presence of ammonia and air it is converted into orceïn, the colouring matter of archil, and becomes coloured a deep reddish violet (Robiquet). Its alkaline solution when heated with a little chloroform becomes coloured first purple-red and then bright red, and on dilution with water has an intense greenish yellow fluorescence, homofluoresceïn, $C_{23}H_{18}O_5$, being formed. This reaction is so delicate that the compounds which yield orcinol can readily be detected in the lichens by its means. A few pieces are boiled with 5 per cent. caustic potash and a little chloroform added to the clear solution; it is then warmed for ten minutes on the water-bath and diluted.[1]

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[1] Lamparter, *ibid.* cxxxiv. 215.

[2] De Luynes, *Ann. Chim. Phys.* [4] vi. 184.

[3] *Ann. Chem. Pharm.* clxv. 366; *Bull. Soc. Chim.* xxi. 373.

[4] *Ber. Deutsch. Chem. Ges.* xv. 2976.

[5] Barth and Hlasiwetz, *Ann. Chem. Pharm.* cxxxiv. 288.

Orcinol may be quantitatively determined by adding standardized bromine water to the dilute solution until tribromorcinol is no longer precipitated and determining the excess of bromine by a solution of potassium iodide.[2]

Orcinol monomethyl ether, $C_6H_3(CH_3)(OCH_3)OH$, is formed, together with the dimethyl ether, when orcinol is boiled with caustic potash, methyl iodide, and wood-spirit. It is a light yellow, oily liquid which boils at 273° and is soluble in alkalis.

Orcinol dimethyl ether, $C_6H_3(CH_3)(OCH_3)_2$, is a yellowish, mobile fluid which boils at 244°, is insoluble in alkalis, and is converted by oxidation into symmetric dimethoxybenzoic acid, or dimethyl-α-resorcylic acid, $C_6H_3(OCH_3)_2CO_2H(5:3:1)$, thus establishing the constitution of orcinol.[3]

Orcinol acetate, $C_6H_3(CH_3)(OC_2H_3O)_2$, is obtained by the action of acetyl chloride on orcinol, and crystallizes from alcohol in needles melting at 25°.[4]

Orcinol diethylcarbonate, $C_6H_3(CH_3)(O.COOC_2H_5)_2$, is obtained by the action of chlorocarbonic ether on the potassium compound of orcinol, and is a thick, oily liquid boiling at 310°—312°.[5]

Orcinolazobenzene, $C_6H_5N{=}NC_6H_2(CH_3)(OH)_2$, is formed when orcinol and diazobenzene nitrate are brought together in aqueous solution. It crystallizes from a mixture of acetic acid and acetic ether in dark red needles melting at 183°.[6]

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[1] Schwarz, *Ber. Deutsch. Chem. Ges.* xiii. 543.

[2] Reymann, *ibid.* viii. 790.

[3] Strong and Tiemann, *ibid.* xiv. 1999.

[4] Luynes and Lionet, *Zeitschr. Chem.* 1867, 561.

[5] Wallach, *Liebig's Ann.* ccxxvi. 86.

[6] Typke, *Ber. Deutsch. Chem. Ges.* x. 1579.

SUBSTITUTION PRODUCTS OF ORCINOL.

2038 These are obtained by the same methods as the corresponding resorcinol compounds, which they resemble very closely.

Chlorine Substitution Products.

			Melting-point.
Trichlororcinol,[1]	$C_6Cl_3(CH_3)(OH)_2$,	long needles	123°
Pentachlororcinol,[2]	$C_6Cl_3(CH_3)(OCl)_2$,	large prisms	120°·5

Bromine Substitution Products.

Monobromorcinol,[3]	$C_6H_2Br(CH_3)(OH)_2$,	crystals	135°
Dibromorcinol,[4]	$C_6HBr_2(CH_3)(OH)_2$,	needles	146°
Tribromorcinol,[5]	$C_6Br_3(CH_3)(OH)_2$,	needles	98°
Pentabromorcinol,[6]	$C_6Br_3(CH_3)(OBr)_2$,	triclinic crystals	126°

Iodine Substitution Products.

Mono-iodorcinol,[7]	$C_6H_2I(CH_3)(OH)_2$,	prisms	80°·5
Tri-iodorcinol,[8]	$C_6I_3(CH_3)(OH)_2$,	brown tablets	—

Nitro-Substitution Products.

α-Nitro-orcinol,[9]	$C_6H_2NO_2(CH_3)(OH)_2$,	golden lustrous needles	120°
β-Nitro-orcinol,	$C_6H_2NO_2(CH_3)(OH)_2$,	dark yellow needles	115°
α-Dinitro-orcinol,[10]	$C_6H(NO_2)_2CH_3(OH)_2$,	deep yellow tablets	164°·5

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[1] Stenhouse, *Proc. Roy. Soc.* 1871.

[2] Stenhouse, Dittler and Liebermann, *Ann. Chem. Pharm.* clxix. 265.

[3] Lamparter, *loc. cit.*

[4] Tiemann and Streng, *loc. cit.*

[5] Stenhouse and Groves, *Journ. Chem. Soc.* 1880, 402.

[6] Stenhouse and Rammelsberg; Dittler and Liebermann, *loc. cit.* 255.

[7] Stenhouse, *Proc. Roy. Soc.* xxii. 53.

[8] Stenhouse, *Journ. Chem. Soc.* 1864, 327.

[9] Weselsky, *Ber. Deutsch. Chem. Ges.* vii. 441.

[10] Stenhouse and Groves, *Journ. Chem. Soc.* 1877, i. 548.

			Melting-point.
β-Dinitro-orcinol,[1]	$C_6H(NO_2)_2CH_3(OH)_2$,	golden yellow needles	109°—110°
Trinitro-orcinol,[2]	$C_6(NO_2)_3CH_3(OH)_2$,	long yellow needles	163·5°

2039 *Archil.* This name was formerly employed to designate both the colouring matter which is extracted from the lichens just mentioned, and the lichens themselves. Theophrastos and Dioscorides mention a plant **φῦκος θαλάσσιον** or **πόντιον**, called by Pliny *Fucus marinus*, which is not a sea-weed, as the name might be taken to imply, but a lichen which grows on the rocks of certain islands, especially Crete, and is capable of dyeing wool a beautiful violet or purple colour.

Archil came into the European market as early as the fourteenth century; the following account of it is given by Beckmann:[3]

Among the oldest and principal Florentine families is that known under the name of Oricellarii or Rucellarii, Ruscellai or Rucellai, several of whom have distinguished themselves as statesmen and men of letters. This family are descended from a German nobleman named Ferro or Frederigo, who lived in the beginning of the twelfth century. One of his descendants in the year 1300 carried on a great trade in the Levant, by which he acquired considerable riches, and returning at length to Florence with his fortune, first made known in Europe the art of dyeing with archil. It is said that a little before his return from the Levant, happening to make water on a rock covered with this lichen, he observed that the plant, which was then called *respio* or *respo*, and in Spain *orciglia*, acquired by the urine a purple, or, as others say, a red colour. He therefore tried several experiments, and when he had brought to perfection the art of dyeing wool with this plant, he made it known at Florence, where he alone practised it for a considerable time to the great benefit of the state. From this useful invention the family received the name Oricellarii, from which at last was formed Rucellai.

[1] Leeds, *Ber. Deutsch. Chem. Ges.* xiv. 483.

[2] Stenhouse, *Proc. Roy. Soc.* xix. 41 ; Merz and Zeller, *Ber. Deutsch. Chem. Ges.* xii. 2038.

[3] Beckmann's *History of Inventions*, vol. i. p. 37.

As several documents, still preserved among the Florentine archives, confirm the above account of the origin of this family name, from the discovery of dyeing with oricello,[1] we may, in my opinion, consider it as certain that the Europeans, and first the Florentines, were made acquainted with this dye-stuff and its use in the beginning of the fourteenth century. At that time the Italians brought from the East the seeds of many arts and sciences, which, afterwards sown and nurtured in Europe, produced the richest harvests; and nothing is more certain than that the art of dyeing was brought to us from the East by the Italians. I do not believe that the merit of having discovered this dye by the above-mentioned accident is due to that Florentine; but I am of opinion that he learned the art in the Levant, and on his return taught it to his countrymen, which was doing them no small service.

The archil lichens, the most valuable of which are *Rocella tinctoria* and *R. fuciformis*, occur in several varieties and in considerable quantity on the coasts of warm and tropical countries, such as the islands of the Mediterranean, the Canary and Cape Verde Islands, Madagascar, Zanzibar, Angola, Ceylon, Java, Peru, Chili, &c.

The old method for the preparation of archil consisted in treating the lichens with stale urine and lime in large casks provided with moveable lids, a considerable quantity of alum and white arsenic being added to prevent the fermentation from passing to a further stage. The mixture is well agitated for a month and then stored in casks in which it is allowed to stand for a long time before use, the colour being found to improve on keeping.

A more modern process consists in treating the finely-chopped lichens with dilute ammonia, and keeping the mixture at the temperature of the air or at a slightly higher one until a dark violet paste has been formed; this is diluted with ammonia and filtered through a press; the solution thus obtained is known as blue archil. Red archil is obtained from this by gentle heating, the ammonia being thus removed.

Stenhouse proposed first to extract the lichens with milk of lime, precipitate the solution with hydrochloric acid and work up the erythrin, &c., thus obtained as by-products, the colouring matter being thus left in a much purer condition. Marnas of Lyons found that the best results were obtained by extracting with dilute ammonia and warming the compounds precipitated from the solution with ammonia in a current of air to 70° for about three weeks. On addition of calcium chloride a precipitate, known as *French purple* (*pourpre française*), is thrown down, and the material thus obtained yields much finer and clearer shades than archil.

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[1] These documents from the Florentine records may be found in *Dominici Mariae Manni de Florentinis Inventis Commentarium.* Ferrariae 1731. Beckmann quotes the passage in question.

Since the discovery of the aniline dyes, archil has lost much of its commercial importance; it is now only used in combination with other colouring matters in order to obtain certain shades of brown, and for the production of a cheap blue for wool dyeing; the material is first grounded with indigo and then dyed with archil, the result being a dye which is similar to that of genuine indigo-blue.

Cudbear or *Persio.* The inhabitants of Sweden, Scotland, Ireland, Wales, &c., have for centuries been in the habit of using various kinds of lichen, especially *Lecanora tinctoria*, for wool-dyeing, the colour being produced by treatment of the lichen with urine. During last century a patent was taken out by Dr. Cuthbert Gordon for the preparation of cudbear,[1] by drying and powdering the pasty mass obtained by the action of ammonia or urine on the lichens. Cudbear is prepared in the Auvergne from *Variolaria orcina* by a similar method.

Orceïn. Robiquet has given this name to the colouring matter of archil, which is formed, as he discovered, by the action of hydrogen and ammonia on orcinol.[2] Gerhardt calculated its formula from the analyses of Dumas and Kane,[3] and gave the following equation for its formation:

$$C_7H_8O_2 + NH_3 + 3O = C_7H_7NO_3 + 2H_2O.$$

Kane prepared orceïn from commercial archil; he describes it as a carmine-red powder, containing carbon and nitrogen in a constant ratio, while the amount of oxygen is variable, being larger as the archil becomes older; hence he assumed that it consists of two similar colouring-matters, α-orceïn and β-orceïn.

Liebermann, who obtained the colouring matter by the action of gaseous ammonia and air on pure orcinol, found that two compounds are thus formed according to the following equations:

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[1] Bancroft, *Philosophy of Permanent Colours*, 1813, i. 300.
[2] *Ann. Chim. Phys.* lviii. 320.
[3] *Ann. Chem. Pharm.* xxxix. 25.

$$2C_7H_8O_2+NH_3+3O=C_{14}H_{11}NO_3+3H_2O$$
$$C_{14}H_{13}NO_4+NH_3+O=C_{14}H_{12}N_2O_3+2H_2O.$$

The latter is therefore formed in larger quantity when the action of the ammonia is allowed to continue for some time; it is less soluble in aqueous ammonia and alcohol than the former compound. Both occur as amorphous masses having a beetle-green lustre, and forming splendid purple solutions with alkalis; but the solution of the second compound has a bluer shade than that of the first.[1]

2040 *Litmus* (*tournesolso Lackmus*) was discovered by the Dutch.[2] It is prepared from various species of *Rocella*, *Variolaria* and *Lecanora*, by allowing them to ferment in contact with ammonia and carbonate of potash, as in the manufacture of archil. When the mass has become violet, stale urine, lime and potashes are added, and the mass again allowed to ferment until it has assumed a blue colour; it is then mixed with gypsum or chalk, and a little indigo,[3] and made up into small tablets.

Kane was the first more accurately to investigate litmus, and he obtained several colouring matters and other substances from it.[4] Wartha, who also investigated the colouring matter of litmus, found indigo in it; this, however, had probably been purposely added as just described, although it may possibly have been derived from the urine, which is known to contain appreciable quantities of a substance which yields indigo on decomposition. On extracting litmus with cold alcohol, Wartha obtained a red colouring matter which is indifferent towards acids, and yields litmus blue and another substance when treated with water. On evaporating the solution and treating the residue with absolute alcohol and a little acetic acid, a scarlet colouring matter is removed, and this is changed to a purple by ammonia, while the pure litmus blue remains behind as a brown powder, which forms a reddish brown aqueous solution turned blue by the slightest trace of an alkali.[5]

According to De Luynes, the pure colouring matter is obtained by digesting 1 part of orcinol with 5 parts of ammonia and 25

[1] *Ber. Deutsch. Chem. Ges.* viii. 1649.

[2] The origin of this name is unknown; it may perhaps be derived from *Lacca musci*, a lake prepared from moss.

[3] Gottlieb, *Chem. Tech.* p. 531.

[4] *Loc. cit.*

[5] *Ber. Deutsch. Chem. Ges.* ix. 217.

parts of crystallized carbonate of soda for four or five days at 60°—80°, and precipitating the solution with hydrochloric acid. It is only slightly soluble in water, and the wine-red colour of this solution is changed to bluish violet by alkalis, and to a reddish brown by acids. It yields a red solution with alcohol, and a yellow one with ether. De Luynes considers that the colouring matter is a weak acid which forms blue salts, the potassium salt existing in litmus.[1]

Litmus is not only employed in the laboratory in the form of litmus paper and tincture, but is also used for colouring wine and vinegar. The colouring matter can readily be recognized by its absorption spectrum; ether extracts it from an acid solution yielding a yellow liquid which absorbs the left end of the spectrum up to E ½ D. A drop of ammonia colours the solution blue, an absorption band being formed which begins at *d*, where it is very intense, gradually diminishing to E. On shaking with water the colouring matter is taken up, and the blue solution gives an absorption band at D; the addition of acid now changes the colour to brick-red, and the solution gives an absorption spectrum similar to that of wine.[2]

Ribbon Litmus (*Tournesollappen, tournesol en drapeaux, Bezetta, Lackmus in Fleckchen*) is obtained in southern France from the expressed sap of *Croton tinctorium*; linen rags are soaked in the sap, dried in the sun, and then exposed on heaps of horse-dung covered with chopped straw, the ammonia evolved being sufficient to change the colour of the rags, which are frequently turned, to blue. They are then again dipped in the sap, to which urine has been added, the colour thus produced becoming dark green or purple-red on drying, and they are then brought into the market. It was formerly believed that the Dutch employed them for the manufacture of litmus, but this is not the case; they are actually used to colour the exterior of cheeses red.

The colouring matter contained in these ribbons has not been accurately investigated; acids change it to red, but the blue colour is not restored by alkalis.

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[1] *Jahresber.* 1864, 551.

[2] Vogel, *Spectralanalyse*, p. 269.

CRESORCINOL, $C_6H_3(CH_3)(OH)_2(1:2:4)$.

2041 This dihydroxytoluene, which was called lutorcin by Vogt and Henninger, may be prepared from β- and γ-amidoparacresol by the diazo-reaction[1] and by fusing bromoparacresol with caustic potash.[2]

It is readily soluble in water, alcohol, ether and benzene, and crystallizes in monosymmetric prisms which form characteristic spherical aggregates and melt at 104°–105°. Ferric chloride produces an unstable, greenish blue colouration, and an alkaline solution becomes coloured red in the air. Like resorcinol it reduces silver solution in the cold, is not precipitated by lead acetate, and gives a precipitate with bromine water which soon becomes crystalline. On heating with phthalic anhydride and dissolving the mass in dilute caustic soda, a solution is formed possessing as fine a green fluorescence as does that obtained by a similar process from resorcinol. It differs however from the latter in yielding no colouring matter when heated with sulphuric acid and nitrobenzene. In presence of ammonia and moist air it is converted into yellow cresorceïn, which dissolves in dilute caustic soda, forming a blue solution turned red by acetic acid.

Isorcinol. Senhofer obtained this compound by the fusion of γ-toluenedisulphonic acid,[3] and Hakansson prepared α-isorcinol in a similar manner from α-toluenedisulphonic acid.[4] Claësson subsequently showed that these two sulphonic acids are identical, and that, therefore, only one isorcinol can exist. It crystallizes in needles melting at 87°–88°, but it resembles cresorcinol so closely that Neville and Winther look upon the two as identical, an opinion which is supported by the fact that the toluenedisulphonic acid has the side chains in the same relation as cresorcinol.

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[1] Knecht, *Ber. Deutsch. Chem. Ges.* xv. 298 and 1069 ; *Ann. Chem. Pharm.* ccxv. 83 ; Wallach, *ibid.* xv. 2831 ; Neville and Winther, *ibid.* xv. 2980.

[2] Vogt and Henninger, *ibid.* xv. 1081.

[3] *Ann. Chem. Pharm.* clxiv. 131.

[4] *Ber. Deutsch. Chem. Ges.* v. 1084.

TOLUQUINOL, OR TOLUHYDROQUINONE.

$C_6H_3(CH_3)(OH)_2(1:2:5)$.

2042 This compound may be obtained from orthotoluidine just as is quinol from aniline,[1] and may also be prepared from β-amido-orthocresol by means of the diazo-reaction.[2] It is readily soluble in water, alcohol and ether, and crystallizes from hot benzene or toluene in pointed, rhombic plates which have a nacreous lustre and melt at 124°. Caustic soda produces a bluish green colouration which rapidly changes to dark brown; bleaching powder solution gives the same reaction, but when very dilute produces a brownish red colour. Oxidizing agents readily convert it into toluquinone.

Toluquinol monomethyl ether, $C_6H_3(CH_3)(OCH_3)OH$, is formed, together with the compound described below, by heating toluquinol with caustic soda, methyl iodide and wood-spirit to 190°. It has a faint smell of creosote, crystallizes in plates melting at 72°, boils at 240°—245°, and yields toluquinone on oxidation.

Toluquinol dimethyl ether, $C_6H_3(CH_3)(OCH_3)_2$, can easily be separated from the monomethyl ether, since it is insoluble in alkalis and non-volatile in steam. It is a liquid which has a pleasant smell like fennel and boils at 214°—218°. When oxidized by chromic acid in acetic acid solution, it is converted into a compound, $C_{16}H_{16}O_4$, which is precipitated by water in brick-red needles and crystallizes from its deep yellow alcoholic solution, in hair-like needles, which appear almost black when seen in masses and become silver-grey on drying. They melt at 153° and sublime when more strongly heated. Ammonium sulphide reduces it to the compound $C_{18}H_{18}O_4$, crystallizing from alcohol in small prisms, melting at 173°, which are readily re-oxidized.

Diacetotoluquinol, $C_6H_3(CH_3)(OCO.CH_3)_2$, is formed by the action of acetyl chloride on toluquinol; it crystallizes from alcohol in large tablets melting at 72° (Nietzki).

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[1] Nietzki, *Ber. Deutsch. Chem. Ges.* x. 834, 1935; *Ann. Chem. Pharm.* ccxv. 158.

[2] Neville and Winther, *Ber. Deutsch. Chem. Ges.* xv. 2979.

TOLUQUINONE, $C_6H_3(CH_3)O_2$.

2043 This compound is formed when paradiamidotoluene,[1] crude cresol[2] or amidorthocresol[3] is oxidized with manganese dioxide and dilute sulphuric acid, or when orthotoluidine hydrochloride is heated with ferric chloride.[4] It crystallizes in small golden-yellow plates which readily volatilize, have a penetrating smell resembling that of benzoquinone, and melt at 69°. It dissolves slightly in cold, more readily in hot water, forming a golden-yellow solution which is coloured brownish red by alkalis. Sulphurous acid reduces it to toluquinol.

Dianilidotoluquinone, $C_6H(CH_3)O_2(NH.C_6H_5)_2$, is obtained by the action of aniline on toluquinone in alcoholic solution; it crystallizes from hot glacial acetic acid in brown, matted needles, which melt at 232°–233° and form a blood-red solution in sulphuric acid. When boiled with alcohol and sulphuric acid, *anilidohydroxytoluquinone*, $C_6H(CH_3)O_2(NH.C_6H_5)OH$, is formed; it crystallizes from alcohol or acetic acid in deep blue needles and forms salts with bases.

Dianilidotoluquinone anilide, $C_6H(CH_3)O(NC_6H_5)(NH.C_6H_5)_2$, is formed when aniline and toluquinone are brought together in solution in a mixture of alcohol and acetic acid. It crystallizes in broad dark-brown plates which have a blue surface lustre, melt at 167° and combine with acids to form salts, which are only slightly soluble in water but crystallize well from alcohol.

On heating with alcoholic sulphuric acid, *anilido-ethoxytoluquinone anilide*, $C_6H(CH_3)O(NC_6H_5)(NH.C_6H_5)OC_2H_5$, is formed; this compound crystallizes from alcohol in silky, red needles melting at 115°—116°, is a tolerably strong base and forms blue salts. It dissolves in concentrated sulphuric acid with a green colour. On treatment with alcoholic potash it yields *anilidohydroxytoluquinone anilide*, $C_6H(CH_3)O(NC_6H_5)(NHC_6H_5)OH$, crystallizing from hot, dilute acetic acid in brownish needles, which form a deep green solution in sulphuric acid. It forms insoluble or difficultly soluble salts with the metals.

Dihydroxytoluquinone, $C_6H(CH_3)O_2(OH)_2$, is obtained from the preceding compound by the action of very dilute caustic potash solution. It is readily soluble in most solvents and crystallizes from them badly; it readily sublimes, however, in brownish yellow, lustrous plates, melting at 177°. Its salts form insoluble or only slightly soluble precipitates which are not characteristic.[1]

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[1] Nietzki, *loc. cit.*
[2] Carstanjen, *Journ. Prakt. Chem.* [2] xxiii. 425.
[3] Nölting and Kohn, *Ber. Deutsch. Chem. Ges.* xvii. 370.
[4] Ladenburg, *ibid.* x. 1125.

Toluquinhydrone, $C_6H_3(CH_3)O_2+C_6H_3(CH_3)(OH)_2$, is obtained by mixing aqueous solutions of the two constituents, and crystallizes in fine, almost black needles which melt at 52° and are tolerably soluble in water forming a brownish yellow solution (Nietzki).

SUBSTITUTION PRODUCTS OF TOLUQUINONE.

The chlorine substitution products are obtained by treating orthocresol or metacresol, and therefore also crude cresol, with potassium chlorate and hydrochloric acid.[2] Trichloroquinone is likewise formed by this method from orthotoluidineparasulphonic acid.[3] Sulphurous acid converts them into the corresponding derivatives of toluquinol.

Dichlorotoluquinone,	$C_7H_4Cl_2O_2$,	yellow transparent tablets.
Trichlorotoluquinone,	$C_7H_3Cl_3O_2$,	yellow plates.
Tetrachlorotoluquinone,	$C_7H_2Cl_4O_2$,	golden, lustrous, scaly crystals.
Tribromotoluquinone,[4]	$C_7H_3Br_3O_2$,	yellow plates.

TOLUQUINONOXIME COMPOUNDS.

2044 *a-Toluquinonoxime*, $C_6H_3(CH_3)O(NOH)$. This compound which is generally known as nitroso-orthocresol, is formed in an analogous manner to quinonoxime (Part III. p. 171) by the action of nitrosyl sulphate on an aqueous solution of orthocresol,[5] or by adding hydroxylamine hydrochloride to a dilute solution of toluquinone.[6] It is only slightly soluble in cold, more readily in hot water, from which it crystallizes in long, white needles, melting at 134°—135°. It forms a reddish brown solution in dilute alkalis, and is thrown down by acids as a white, flocculent precipitate.

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[1] Hagen and Zincke, *Ber. Deutsch. Chem. Ges.* xvi. 1558.

[2] Southworth, *Ann. Chem. Pharm.* clxviii. 274; Bergmann, *ibid.* clii. 248; Bräuninger, *ibid.* clxxxv. 352; Knapp and Schultz, *ibid.* ccx. 176.

[3] Hayduck, *ibid.* clxxii. 209.

[4] Canzoneri and Spica, *Ber. Deutsch. Chem. Ges.* xvi. 793.

[5] Nölting and Kohn, *ibid.* xvii. 370.

[6] Goldschmidt and Schmidt, *ibid.* xvii. 2063.

Potassium α-toluquinonoximate, $C_6H_3(CH_3)O(NOK)$, is obtained by the addition of an ethereal solution of toluquinoneoxime to a solution of potassium ethylate, as a yellowish green precipitate, which crystallizes from acetone in brown needles.

Sodium α-toluquinonoximate, $C_6H_3(CH_3)O(NONa)+3H_2O$, is a dark green precipitate which crystallizes from acetone in short, brown needles, and forms a reddish brown solution in water; it detonates when heated.

Toluquinonoxime gives Liebermann's reaction with phenol and sulphuric acid; potassium ferricyanide oxidizes it to β-nitro-orthocresol, and nitric acid to dinitro-orthocresol, while it is converted into β-amido-orthocresol by reduction.

α-Toluquinone chlorimide, $C_6H_3(CH_3)O(NCl)$, is formed in an analogous manner to quinone chlorimide when a concentrated solution of bleaching powder is added to a dilute hydrochloric acid solution of γ-amido-orthocresol; the liquid first becomes coloured cherry-red, changing to golden-yellow, the chlorimide then separating out. It crystallizes from benzene in yellow needles, which melt at 87°—88° and detonate at higher temperatures. When boiled with water it volatilizes, a portion being simultaneously decomposed into α-toluquinone and brown, amorphous bodies; it also gives Liebermann's reaction.[1]

β-Toluquinonoxime, or *Nitrosometacresol*, $C_6H_3(CH_3)O(NOH)$, has been prepared by boiling nitrosodimethylmetatoluidine; it is slightly soluble in hot water, from which it crystallizes in small, colourless needles, while it is deposited from solution in ether or acetic acid in thick needles or prisms, decomposing at 140°—150°.

β-Toluquinonoxime acetate, $C_6H_3(CH_3)O(NO.C_2H_3O)$, is obtained by the action of acetic anhydride on the compound just described; it crystallizes from alcohol in prisms melting at 92°.

β-Toluquinonoxime gives Liebermann's reaction in a most characteristic manner; nitric acid oxidizes it to trinitrometacresol.[2]

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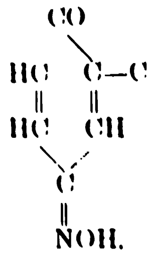
[1] Hirsch, *Ber. Deutsch. Chem. Ges.* xviii. 1514.

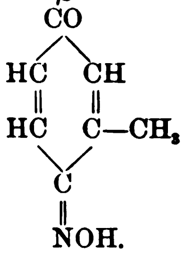
[2] Wurster and Riedel, *ibid.* xii. 1799.

The following formulæ explain the isomerism of the two toluquinonoximes :

α

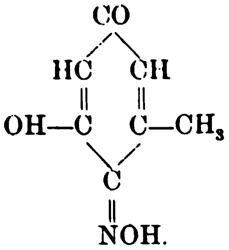


β



Paracresol does not form a nitroso-compound or quinonoxime, since the methyl group is situated in the para-position.

Hydroxytoluquinonoxime, $C_6H_2(CH_3)(OH)O(NOH)$. This compound, which is also called nitroso-orcinol, is obtained by evaporating a solution of 12 grammes of orcinol and 4 grammes of caustic soda to a syrup, and gradually adding 12 grammes of amyl nitrite to the cold mass with constant stirring; the mixture is then gently heated on the water-bath until a small portion dissolved in water gives a red precipitate with sulphuric acid. The fused mass is then dissolved in water and precipitated with dilute sulphuric acid. Nitroso-orcinol crystallizes from alcohol in small dark red prisms, which become coloured black at 110° without melting.[1] It has the following constitution :



Azo-orcin, $C_{14}H_{11}NO_3$. Weselsky obtained this compound by the action of his reagent on an ethereal solution of orcinol;[2] it is also formed when orcinol is heated on the water-bath with nitroso-orcinol and sulphuric acid (Brunner and Krämer). It crystallizes in small, brownish red prisms which dissolve in alkalis forming a deep purple-coloured solution with a splendid orange-red fluorescence; acids precipitate it from this as a scarlet powder.

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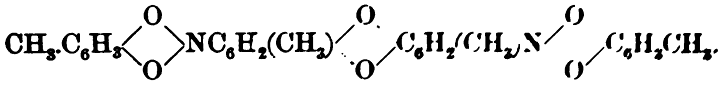
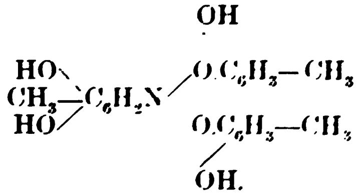
[1] Brunner and Krämer, *Ber. Deutsch. Chem. Ges.* xvii. 1879.

[2] *Ibid.* vii. 439.

Its formation is quite analogous to that of azoresorcin, $C_{12}H_9NO_4$ (Part III. p. 176), but it is not homologous with this substance. The homologous compound is, however, first formed and is converted into azo-orcin with loss of water; the latter compound may probably possess the following constitution:



Liebermann obtained a similar colouring matter by gradually adding 40 grammes of his reagent to a solution of 10 grammes of orcinol in 10 grammes of sulphuric acid.[1] Another colouring matter is simultaneously formed but can easily be separated, as it forms a sodium salt which is insoluble in alcohol, while that of the former forms a purple-red solution with a cinnabar-red fluorescence. The colouring matter, $C_{22}H_{21}NO_6$, separated from this solution by the addition of an acid, is an amorphous mass with a beetle-green fluorescence, the aqueous alkaline solution of which has a brownish red fluorescence. The formation of this compound corresponds exactly to that of Liebermann's phenol colouring-matter, and its constitution is therefore the following:



The second colouring matter, $C_{22}H_{21}NO_7$, is an oxidation product of the former, which it resembles very closely; its violet alkaline solution, however, does not fluoresce (Brunner and Krämer).

TRIHYDROXYTOLUENES, $C_6H_2(CH_3)(OH)_3$.

2045 *Methylpyrogallol*, or *Methylpyrogallic acid*, is the only known compound of this group. Its dimethyl ether occurs, together with the same ethers of pyrogallol and propylpyrogallol in the fraction of beech-wood-tar creosote which dissolves in alkalis and boils at between 255° and 270°. In order to separate them, the mixture is heated with benzoyl chloride, the benzoic ethers separated by fractional crystallization and then decomposed by alcoholic potash.

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[1] *Ber. Deutsch. Chem. Ges.* vii. 1110.

Methylpyrogallol dimethyl ether, $C_6H_2(CH_3)(OCH_3)_2OH$, is a crystalline substance, melts at 36°, and boils at 265°. On heating with concentrated hydrochloric acid, methylpyrogallol is obtained; this closely resembles pyrogallol, and on heating sublimes in needles, which melt at 129°. Its aqueous solution is coloured brown by ferrous sulphate, and its alkaline solution rapidly turns brown in the air.[1]

AMIDO-DERIVATIVES OF TOLUENE.

AMIDOTOLUENES, OR TOLUIDINES, $C_6H_4(CH_3)NH_2$.

2046 The history of these compounds goes hand in hand with that of the nitrotoluenes. Hofmann and Muspratt reduced crude nitrotoluene by repeated treatment with alcoholic ammonium sulphide and obtained the product free from unaltered nitrotoluene by washing well with water, treating with hydrochloric acid and distilling the liquid, after the removal of all alcohol by evaporation, with caustic soda; they thus obtained an oily liquid which solidified after some time to a crystalline mass, and to this new organic base they gave the name *toluidine*. The aqueous distillate obtained in the preparation contained some ammonia and a not inconsiderable amount of base in solution; the whole distillate was therefore treated with an excess of ammonium oxalate, evaporated to dryness on the water-bath and the residue extracted with boiling absolute alcohol, ammonium oxalate being in this way left undissolved. On cooling, toluidine oxalate separated out in white crystals, which were washed, dissolved in hot water, and decomposed with concentrated caustic potash solution. The oil which separated out solidified on cooling to a radiating crystalline mass of pure toluidine, the properties of which were then accurately investigated.

After the discovery of the aniline dyes, aniline and toluidine,

[1] Hofmann, *Ber. Deutsch Chem. Ges.* xii. 1371.

or rather a mixture of the two called *aniline oil*, was manufactured on the large scale; and Rosenstiehl found in this mixture a liquid base, isomeric with the ordinary toluidine, to which he gave the name of *pseudotoluidine*. We have already pointed out that the three nitrotoluenes are formed in varying quantities by the nitration of toluene. If concentrated acid be employed without cooling, paranitrotoluene is chiefly formed, and this yields on reduction the solid paratoluidine obtained by Hofmann and Muspratt. If, however, a weaker acid be employed, and the temperature be kept low, more of the ortho-compound is formed, and it is from this that the pseudotoluidine is derived; a small quantity of metanitrotoluene being, however, invariably produced.

The toluidines are manufactured on a large scale; the para-compound is that which is most readily obtained in the pure state, as the purification of paranitrotoluene offers no difficulties, whilst it is very difficult, working on the large scale, to obtain an orthonitrotoluene free from paranitrotoluene, so that ordinary commercial orthotoluidine always contains some of the para-compound together with metatoluidine and generally a little aniline.

The amount of paratoluidine in such a mixture can readily be determined by means of the different solubilities of the oxalates in ether; at 15°

Acid paratoluidine oxalate requires 6660 parts of ether,
Acid orthotoluidine oxalate „ 200 „

for solution. A small quantity, about 0·2 grms., of the mixture is dissolved in 80 grms. of ether and titrated with a solution of 1·062 grms. of oxalic acid in 250 c.c. of ether until no further precipitate is formed. Each cubic centimetre of the solution employed corresponds to 0·005 grms. of paratoluidine.[1] The end of the reaction can easily be recognised by the acid reaction of the solution towards litmus-paper as soon as the orthotoluidine oxalate commences to be formed. The determination is rendered still more accurate by adding an excess of oxalic acid solution to the solution of the bases, filtering from the precipitate, evaporating the ether, dissolving the residue in a little water and determining the excess of oxalic acid by decinormal caustic soda solution.[2]

[1] Rosenstiehl, *Ann. Chim. Phys.* (1872), xxvi. 249.
[2] Lorenz, *Ann. Chem. Pharm.* clxxii. 190.

In order to separate larger quantities of the base, an amount of oxalic or sulphuric acid equivalent to the paratoluidine present is added, and the whole distilled with steam; orthotoluidine alone passes over, and the para-compound as the stronger base remains behind in combination with the acid (Rosenstiehl).

Ihle dissolves the bases in ether, precipitates with an ethereal solution of oxalic acid and from time to time treats a small portion of the solution with acetyl chloride. The product is re-crystallized from hot water and its melting-point observed. Since acetparatoluide melts at 145°, and acetorthotoluide at 107°, the point at which all the paratoluidine is removed can readily be recognised.[1]

Binschedler gives the following process for the treatment of a mixture of 30 per cent. of paratoluidine and 70 per cent. of orthotoluidine which comes into the market under the name of "*aniline lourde spéciale*": 10 kilos. of the mixture of bases are gradually added to a solution of 2·5 kilos. of oxalic acid in 25 litres of boiling water to which 6 litres of hydrochloric acid of specific gravity 1·15 have been added, the mixture being then heated to the boiling point, and constantly stirred until it has cooled down again to 60°. The crystalline precipitate which consists of pure paratoluidine oxalate, is rapidly filtered off, pressed, and washed with a little water; 2 kilos. of oxalic acid are now added to the filtrate, a mixture of the oxalates being thus precipitated. When oxalic acid produces no further precipitate in the mother-liquor, it is distilled with caustic soda, orthotoluidine being obtained which contains a very small quantity of paratoluidine and only traces of aniline.[2]

Another method of separation, which has been patented by Leo Levy, depends upon the behaviour of the hydrochlorides of the bases towards sodium phosphate. Aniline hydrochloride gives the following reaction:

$$Na_2HPO_4 + 2C_6H_5NH_3Cl = 2NaCl + (C_6H_5.NH_3)_2HPO_4.$$

Paratoluidine hydrochloride behaves in a similar manner, while the orthotoluidine salt yields 80 per cent. of the free base and 20 per cent. of the acid phosphate:

1) $C_7H_7.NH_2HCl + Na_2HPO_4 = C_7H_7.NH_2 + NaH_2PO_4 + NaCl.$
2) $C_7H_7.NH_2HCl + NaH_2PO_4 = (C_7H_7.NH_3)H_2PO_4 + NaCl.$

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[1] *Journ. Prakt. Chem.* [2] xiv. 449.

[2] *Ber. Deutsch. Chem. Ges.* vi. 448.

The mixed hydrochlorides are therefore treated with a solution of sodium phosphate; the crystalline mass which is formed is then dissolved by warming, and the orthotoluidine removed from the surface. On cooling, the phosphates of aniline and paratoluidine separate out completely, while the phosphate of orthotoluidine remains in solution. The sodium phosphate can be recovered after separation of the bases; sodium arsenate may also be employed.[1]

Another process for the separation of orthotoluidine from aniline oil by means of the nitrate has been described by L. Schad.[2]

2047 *Orthotoluidine*, discovered by Rosenstiehl,[3] is formed by the reduction of orthonitrotoluene and by the distillation of paramidotoluic acid with lime.[4] It is a colourless liquid resembling aniline very closely; it soon becomes brown in the air or on exposure to light, boils at 198·5°, has a specific gravity of 1·003 at 20·2°, and does not solidify at −20°. A solution of this base in monohydrated sulphuric acid gives a blue colouration with a solution of chromium trioxide in sulphuric acid of the same strength; the colour changes to a stable reddish violet on dilution. Nitric acid added to the sulphuric acid solution gives an orange to brown colouration, passing into yellow on the addition of water. If the base be dissolved in ether and an equal volume of water added, the lower layer of the solution gives a yellow to brown colouration with dilute sulphuric acid. If the ethereal layer be now removed and shaken with dilute sulphuric acid, it becomes coloured a stable reddish violet (Lorenz).

Orthotoluidine further differs from its isomerides in giving a green colouration with ferric chloride and a little paradiamidobenzene. This reaction is so delicate that a solution containing 1 in 10,000 gives a tolerably deep colouration, and a solution only one-tenth as strong as this assumes a distinct shade of green.[5] All commercial aniline gives this reaction, as also does that obtained by the distillation of indigo with caustic potash, which was considered to be chemically pure until Rosenstiehl proved that it contained orthotoluidine.

The salts of orthotoluidine have been investigated by Beilstein and Kuhlberg.

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[1] *Ber. Deutsch. Chem. Ges.* xvi. 980.

[2] *Ibid.* vi. 1361.

[3] *Zeitschr. Chem.* [2] iv. 557.

[4] Beilstein and Kuhlberg, *Ann. Chem. Pharm.* clvi. 75.

[5] Monnet, Reverdin and Nölting, *Ber. Deutsch. Chem. Ges.* xi. 2278. See also Reinhardt and Städel, *ibid.* xv. 29.

Orthotoluidine hydrochloride, $C_7H_9NClH+H_2O$, forms white crystalline crusts, 37·4 parts of which dissolve in 100 parts of water at 15·5°; it is still more readily soluble in alcohol.

Orthotoluidine hydrobromide, $C_7H_9N.BrH$, crystallizes very easily in large rhombic prisms; the hydriodide resembles it, but is partially decomposed by water.[1]

Orthotoluidine sulphate, $(C_7H_9N)_2H_2SO_4$, forms small crystals which become coloured violet to green in the air; 100 parts of water at 22° dissolve 7·5 parts. It is only slightly soluble in alcohol.

Orthotoluidine nitrate, $C_7H_9N.HNO_3$, crystallizes in small plates; 100 parts of water at 19·2° dissolve 10·01 parts.

Orthotoluidine oxalate crystallizes in small colourless plates; 100 parts of water at 21° dissolve 2·38 parts.

Methylorthotoluidine, $C_6H_4(CH_3)N(CH_3)H$, is formed when 750 grms. of orthotoluidine are heated for a day to 200°—220° with 400 grms. of methyl alcohol and 700 grms. of hydrochloric acid. The product is distilled in steam, and every 100 grms. of distillate dissolved in 120 grms. of hydrochloric acid and 300 grms. of water, the solution being then treated with a concentrated solution of 40 grms. of sodium nitrite, the mixture being cooled and well agitated. The *methylorthotolylnitrosamine*, $C_6H_4(CH_3)N(CH_3)NO$, formed, which is very similar to methylnitroso-aniline, is extracted with ether, reduced with tin and hydrochloric acid, decomposed with caustic soda, and distilled with steam.

Methylorthotoluidine is a colourless liquid which rapidly becomes coloured violet-brown in the air, and boils at 207°—208°.[2]

Dimethylorthotoluidine, $C_6H_4(CH_3)N(CH_3)_2$. Thomsen obtained this compound by the distillation of trimethyltolylammonium hydroxide; it is also formed, together with other products, when trimethylphenylammonium iodide is heated to 220°—230°.[3] It can readily be prepared pure by heating 750 grms. of orthotoluidine for two days with 670 grms. of methyl alcohol and 700 grms. of hydrochloric acid, the product being repeatedly rectified (Monnet, Reverdin and Nölting). It is a colourless liquid which has a characteristic aromatic odour and boils at 183°.

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[1] Städel, *Ber. Deutsch. Chem. Ges.* xvi. 28.

[2] Monnet, Reverdin and Nölting, *Ber. Deutsch. Chem. Ges.* xi. 2278. See also Reinhardt and Städel, *ibid.* xv. 29.

[3] Hofmann, *ibid.* x. 1585.

Trimethylorthotolylammonium iodide, $C_6H_4(CH_3)N(CH_3)_3I$, is formed by the continued action of methyl iodide on orthotoluidine,[1] and crystallizes in large needles which assume a faint purple tint in the air.

			Boiling-point.
Ethylorthotoluidine,	$C_7H_9N(C_2H_5)H$,	liquid	213°—214°
Diethylorthotoluidine,[2]	$C_7H_9N(C_2H_5)_2$	„	208°—209°.

Phenylorthotolylamine, $C_6H_5.NH(C_7H_7)$, is formed, together with diphenylamine and di-orthotolylamine, when orthotoluidine is heated with aniline hydrochloride to 280°.[3] It is a crystalline substance which melts at 41°, boils at 297°—299°, and gives a violet-blue colouration with nitric acid.

Di-orthotolylamine, $(C_7H_7)_2NH$, is a liquid boiling at 304°—308°.

Acetorthotoluide, $C_7H_7.N(C_2H_3O)H$, forms long needles, melts at 107° and boils at 296°; 100 parts of water at 19° dissolve 0·86 parts (Beilstein and Kuhlberg).

Orthotolyl carbamide, $(C_7H_7)NH.CO.NH_2$, is formed by the action of potassium cyanate on orthotoluidine hydrochloride; it is insoluble in cold water, moderately soluble in hot water, and readily in alcohol, crystallizing in tablets which melt at 185°.[4]

Di-orthotolyl carbamide, $(C_7H_7)_2NCO.NH_2$, is formed by the action of carbonyl chloride on orthotoluidine, by heating the latter with urea,[5] or by heating its hydrochloride with cyanamide to 100°.[6] It is insoluble in water, but slightly soluble in alcohol, crystallizing in fine needles which melt at 243°.

Orthotolyl carbamide, or *Orthotolyl isocyanate*, $CON.C_6H_4.CH_3$. When orthotoluidine is acted upon by chlorocarbonic ether, *orthotolyl urethane*, $NH(C_7H_7)CO.OC_2H_5$, is formed in crystals melting at 46°,[7] and on heating with phosphorus pentoxide is converted into the isocyanate, which is a liquid boiling at 186° and possessing a penetrating odour (Girard). Water decomposes it with formation of ditolyl carbamide.

Orthotolyl thiocarbamide, $(C_7H_7)HN(CS)NH_2$, is obtained by the action of ammonia on orthotolyl mustard oil; it melts at 155° and is readily soluble in boiling water.[8]

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[1] Thomsen, *Ber. Deutsch. Chem. Ges.* x. 1586.

[2] Stadel and Reinhardt, *loc. cit.*; Norton, *Ann. Chem. Journ.* vii. 118.

[3] Girard and Willm, *Bull. Soc. Chim.* xxv. 248.

[4] Cosack, *Ber. Deutsch. Chem. Ges.* xiii. 1089.

[5] Girard, *ibid.* vi. 444.

[6] Berger, *ibid.* xii. 1859.

[7] Lachmann, *ibid.* xii. 1349; Neville and Winther, *ibid.* xii. 2324.

[8] Staats, *ibid.* xiii. 135.

Di-orthotolyl thiocarbamide, $(C_7H_7.NH)_2CS$, is obtained by the action of carbon disulphide on an alcoholic solution of orthotoluidine.[1] It crystallizes from hot alcohol in needles melting at 158°.

Orthotolyl thiocarbamide, or *Orthotolyl mustard oil*, $CSN.C_6H_4.CH_3$, is formed when the compound just described is boiled with fuming hydrochloric acid. It is a strongly refractive liquid, boiling at 239° and possessing a pungent odour (Girard).

It combines with aniline forming *phenylorthotolyl thiocarbamide*, $(C_6H_5)NH(CS)NH(C_7H_7)$, which has also been prepared from orthotoluidine and phenyl mustard oil (Staats); it forms long needles melting at 139°, and is decomposed by hydrochloric acid into aniline and tolyl mustard oil.

2048 *Metatoluidine* was obtained by Beilstein and Kuhlberg by the reduction of metanitrotoluene,[2] which is best effected by means of stannous chloride and hydrochloric acid (Cosack). According to Widmann, it is also formed when metanitrobenzylene chloride, $C_6H_4(NO_2)CHCl_2$, obtained by the action of phosphorus chloride on metanitrobenzaldehyde, is reduced with zinc dust and hydrochloric acid.[3]

It is a colourless oily liquid which has a specific gravity of 0·998 at 25°, and becomes converted into a brown resinous mass when exposed to the air (Lorenz); it boils at 197° and does not solidify even at −13°. If it be dissolved in monohydrated sulphuric acid and treated with a sulphuric acid solution of chromium trioxide, a yellowish brown liquid is obtained which becomes brown on gentle heating, and is coloured greenish yellow by the addition of a little water, a larger quantity rendering it colourless. Nitric acid added to the original solution produces a reddish colouration which rapidly becomes a deep blood-red, and then a dark dirty-red, and is converted into orange by the addition of water. When a solution of the base in equal volumes of ether and water is treated with bleaching powder solution, the aqueous layer is coloured brownish yellow and becomes turbid, while the ether exhibits a reddish fluorescence; if the ether be poured off and shaken up with water and a drop of dilute sulphuric acid, the water becomes coloured a faint violet.

The salts of metatoluidine have been investigated by Lorenz.[4]

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[1] Girard, *Ber. Deutsch. Chem. Ges.* iv. 985; Berger, *ibid.* xii. 1854.

[2] *Ann. Chem. Pharm.* clvi. 83.

[3] *Ber. Deutsch. Chem. Ges.* xiii. 676; xiv. 2583. See also *ibid.* xiv. 1403.

[4] *Ann. Chem. Pharm.* clxxii. 177.

Metatoluidine hydrochloride, $C_7H_9N.ClH$, crystallizes from a very concentrated aqueous solution in thin tablets, and from alcohol in thin, pale red crusts.

Metatoluidine sulphate, $(C_7H_9N)_2SO_4H_2$, crystallizes in long, transparent, light red, radiating needles, which are insoluble in ether, slightly soluble in alcohol, and more readily in water, 100 parts of which at 14° dissolve 6·25 parts.

Metatoluidine nitrate, $C_7H_9N.NO_3H$, crystallizes in large, pale red, rhombic plates, 16·42 parts of which dissolve in 100 parts of water at 15·5°; it is still more soluble in alcohol, but only slightly soluble in ether.

Acid metatoluidine oxalate, $C_7H_9N.C_2O_4H_2$, forms warty masses consisting of fine silky needles, which are only slightly soluble in ether, alcohol and water; 100 parts of the latter at 13° dissolve 2·65 parts. When its solution is warmed with metatoluidine, the salt, $(C_7H_9N)_3(C_2O_4H_2)_2$, separates out in a mass of rhombic plates which are still less soluble than the monoacid salt. If an excess of metatoluidine be added in warm alcoholic solution to oxalic acid, small rhombic plates separate out on cooling in such quantity that the liquid solidifies to a jelly. These crystals appear to be the hydrated normal salt; after washing with alcohol and drying, they possess the appearance of cholesterin; they are scarcely wetted by water and when heated with it for a long time decompose into the acid salt and the free base.

Methylmetatoluidine, $C_6H_4(CH_3)N(CH_3)H$, is formed, together with dimethylmetatoluidine, by the action of methyl iodide on the primary base. The product is extracted with ether and freed from unattacked metatoluidine by the addition of sulphuric acid, an alkali is then added, the ether distilled off and the residual oil dried and heated with acetic anhydride. On distillation, acetic acid and acetic anhydride first come over, followed by dimethyltoluidine and finally by methylacetoluide, boiling above 250°. This is purified by repeated distillation and decomposed by heating with dilute sulphuric acid, pure methylmetatoluidine being thus obtained; it is a colourless liquid which boils at 206°—207°, and possesses a characteristic aromatic odour.

Dimethylmetatoluidine, $C_6H_4(CH_3)N(CH_3)_2$, boils at 215° (Wurster and Riedel), and has a characteristic odour differing from that of its isomerides, but resembling that of dimethylaniline.[1]

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[1] Nölting, *Ber. Deutsch. Chem. Ges.* xi. 2278.

Nitrosodimethylmetatoluidine, $C_6H_3NO(CH_3)N(CH_3)_2$, is formed on the addition of sodium nitrite to a cooled solution of dimethylmetatoluidine in hydrochloric acid. The hydrochloride thus prepared crystallizes from a hot, acidified solution in light yellow to greenish yellow needles which are only slightly soluble in cold water. Sodium carbonate liberates the free base, which crystallizes from ether in small, green plates or long needles, melting at 92°. It is precipitated by petroleum ether from a solution in chloroform in moss-green needles, and separates from benzene in large, dark green crystals containing benzene of crystallization, which they lose in the air together with their colour and lustre. All its solutions are coloured deep green. It crystallizes from water in small, lustrous green plates.

Like nitrosodimethylaniline, it forms deep steel-blue coloured compounds with aniline, orthotoluidine, &c., and does not give Liebermann's reaction in the cold. Boiling dilute caustic soda converts it into nitrosocresol; potassium permanganate oxidizes it to *nitrodimethylmetatoluidine*, $C_6H_3NO_2(CH_3)N(CH_3)_2$, which crystallizes in long yellow needles, melting at 84°. It is reduced by tin and hydrochloric acid to *dimethyldiamidotoluene* $C_6H_2(CH_3)(NH_2)N(CH_3)_2$.

Since the two isomerides of dimethyltoluidine give no nitroso compounds, the presence of metatoluidine can readily be detected in orthotoluidine, and its amount approximately determined; to effect this the hydrochlorides are prepared, the greater part of the orthotoluidine salt removed by crystallization, the mother-liquor evaporated to dryness, and the residue heated with methyl alcohol; the almost insoluble nitrosodimethylmetatoluidine is then prepared directly from the mixture of dimethyltoluidines thus obtained. The two bases can also be separated by fractional distillation, since the ortho-compound boils at 183° and the meta-compound at 215°.[1]

Metaditolylamine, $(C_6H_4.CH_3)_2NH$, is formed when metatoluidine is heated with its hydrochloride. It is a thick, oily, light yellow liquid which becomes coloured brown in the air and boils at 319°—320°.[2]

Acetmetatoluide, $C_6H_4(CH_3)N(C_2H_3O)H$, crystallizes on the gradual evaporation of its aqueous solution in long needles united to form bushy aggregates; it melts at 65·5°, and boils at

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[1] Wurster and Riedel, *Ber. Deutsch. Chem. Ges.* xii. 1796.

[2] Cosack, *ibid.* xiii. 1088.

303°. 100 parts of water at 13° dissolve 0·44 parts (Beilstein and Kuhlberg).

Metatolyl carbamide, $(C_6H_4.CH_3)HN.CO.NH_2$, has been prepared from metatoluidine and potassium cyanate; it crystallizes from water in small plates, and from alcohol in tablets or needles, melting at 142°.

Dimetatolyl carbamide, $CO(NH.C_7H_7)_2$. When metatoluidine is acted upon by chlorocarbonic ether, *metatolyl urethane*, $(C_7H_7)HN.CO.OC_2H_5$, is formed; this is a liquid which on distillation in the moist state yields alcohol, carbon dioxide, and dimetatolyl carbamide. The latter crystallizes from hot alcohol in long needles melting at 217° (Cosack).[1]

Metatolyl thiocarbamide, $(C_7H_7)HN.CS.NH_2$, is obtained by the action of ammonia on metatolyl thiocarbimide. It is readily soluble in alcohol, slightly in cold, and more freely in hot water, and crystallizes in prisms which form star-shaped aggregates, and melt at 103°.[2]

Dimetatolyl thiocarbamide, $CS(NH.C_7H_7)_2$, is formed when an alcoholic solution of metatoluidine is heated for a long time with carbon disulphide. It crystallizes in concentrically arranged needles, melting at 122°, which are scarcely soluble in boiling water but dissolve readily in alcohol.

Metatolyl thiocarbamide, or *Metatolyl mustard oil*, $CSN(C_6H_4.CH_3)$, is formed when the compound just described is heated with concentrated hydrochloric acid. It is a colourless liquid which boils at 244° and possesses the characteristic smell of the mustard oils in the highest degree (Weith and Landolt.)

2049 *Paratoluidine* is formed by the reduction of paranitrotoluene and by heating methylaniline hydrochloride for a day to 350°; methylaniline hydriodide, on the other hand, gives a liquid toluidine,[3] which is probably the ortho-compound. It may also be obtained by heating paracresol with the compound of zinc chloride and ammonia to 300°.[4] It is slightly soluble in water, readily in alcohol and ether, and crystallizes from hot, dilute alcohol in large, colourless plates which melt at 45° and have a peculiar aromatic odour resembling that of aniline. According to Hofmann and Muspratt it boils at 198°, while Städeler found its boiling-point to be 204°—206°.[5] When it is dissolved in monohydrated sulphuric acid and treated with a solution of chromium trioxide in acid of the same strength, it is only coloured yellow. A drop of nitric acid added to the original solution produces a blue colouration, which soon passes through violet and red to brown (Lorenz); in presence of aniline or orthotoluidine no blue colouration is produced, but the liquid becomes coloured blood-red. Bleaching powder solution gives no colouration with solutions of pure paratoluidine; in order therefore to detect the presence of aniline in paratoluidine, the mixture is dissolved in ether, and shaken up with an equal volume of water, a solution of bleaching powder then being added drop by drop. If aniline be present, the ether assumes a blue colour when the solution is agitated (Rosenstiehl).

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[1] *Ber. Deutsch. Chem. Ges.*; see also xii. 1450.

[2] Weith and Landolt, *ibid.* viii. 715.

[3] Hofmann, *ibid.* v. 720.

[4] Buch, *ibid.* xiv. 2345; xvii. 2637.

[5] *Jahresber.* 1865, 409.

The salts of paratoluidine have been investigated by Hofmann and Muspratt and by Beilstein and Kuhlberg.[1]

Paratoluidine hydrochloride, C_7H_9N,HCl, crystallizes in white crusts, which become coloured in the air. 100 parts of water at 11° dissolve 22·9 parts, while 100 parts of 89 per cent. alcohol dissolve 25 parts at 17°.

Paratoluidine hydrobromide, C_7H_9N, HBr, crystallizes in white plates; the hydriodide is very similar (Reinhardt and Städel).

Paratoluidine sulphate, $(C_7H_9N)_2H_2SO_4$, forms lustrous, scaly crystals, 5·06 parts of which dissolve in 100 parts of water at 22°; they are still less soluble in alcohol.

Paratoluidine nitrate, C_7H_9N, HNO_3, crystallizes, when its solution is rapidly cooled, in large rhombic tablets; when allowed to deposit more gradually, it forms long, transparent needles. 100 parts of water at 23·5° dissolve 17·7 parts; it is still more readily soluble in alcohol.

Acid paratoluidine oxalate, $C_7H_9N, C_2O_4H_2$, crystallizes in rhombic needles or prisms, 0·87 parts of which dissolve in 100 parts of water at 14°; alcohol takes up even less.

Paratoluidine phenate, C_7H_9N, C_6H_6O, crystallizes from petroleum ether in long needles melting at 31·1°.[2]

Methylparatoluidine, $C_6H_4(CH_3)N(CH_3)H$, is obtained by passing methyl chloride into heated paratoluidine. The product is extracted with ether, the paratoluidine hydrochloride formed being left undissolved. Any unaltered paratoluidine is precipitated by dilute sulphuric acid, and the ether evaporated, a mixture of methyltoluidine and dimethyltoluidine being thus obtained. The former is converted by the action of acetic anhydride into *acetmethylparatoluide*, $C_6H_4(CH_3)N(C_2H_3O)CH_3$, which crystallizes from a mixture of ether and alcohol in large plates melting at 83°. Pure methylparatoluidine is then obtained by boiling this compound with hydrochloric acid and decomposing the hydrochloride with caustic soda.[1] It can be even more simply separated by means of its nitrosamine, in the same way as its isomeride in the ortho-series. (Monnet, Reverdin and Nölting.) It is a liquid which boils at 208° and possesses an aromatic odour.

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[1] *Ann. Chem. Pharm.* clvi. 73.

[2] G. Dyson, *Journ. Chem. Soc.* 1883, i. 468.

Nitrosomethylparatoluidine, $C_6H_4(CH_3)N(CH_3)NO$, crystallizes from a mixture of ether and alcohol in large, well-formed prisms, melting at 54°.

Dimethylparatoluidine, $C_6H_4(CH_3)N(CH_3)_2$. By the action of methyl iodide on paratoluidine, Thomsen obtained *trimethylparatolylammonium iodide*, $C_7H_7N(CH_3)_3I$, which forms white crystals, and converted it by means of moist silver oxide into the hydroxide, which yielded the base on distillation;[2] it is a liquid, which has a characteristic aromatic odour and boils at 208°.

			Boiling-point.
Ethylparatoluidine,	$C_7H_7N(C_2H_5)H$,	liquid	217°
Di-ethylparatoluidine,[3]	$C_7H_7N(C_2H_5)_2$	„	229°

Phenylparatoluidine, or *Phenylparatolylamine*, $C_7H_7N(C_6H_5)H$, was obtained by Hofmann by the dry distillation of toluidine-blue or tritolylrosaniline,[4] while de Laire, Girard, and Chapoteau prepared it by heating aniline with toluidine hydrochloride or toluidine with aniline hydrochloride. In both cases the product is a mixture of diphenylamine, phenyltoluidine, and ditolylamine, which cannot be readily separated by fractional distillation.[5]

It is also formed when equal molecules of phenol and paratoluidine, or paracresol and aniline, are heated with an excess of zinc chloride for twenty hours to 260°—300°.[6] Phenylparatoluidine crystallizes readily from alcohol in long, silky needles, melts at 87° and boils at 334·5°. Its salts, like those of diphenylamine, are decomposed by water, and it gives a fine blue colouration with concentrated nitric acid. When fused with mercuric chloride or hexchlorethane, a splendid violet colouring matter is formed.

[1] Thomsen, *Ber. Deutsch. Chem. Ges.* x. 1582.

[2] See also Hübner, Tölle and Athenstädt, *Ann. Chem. Pharm.* ccxxiv. 336.

[3] Morley and Abel, *ibid.* 93, 313.

[4] *Ibid.* cxxxii. 291.

[5] Buch, *Ber. Deutsch. Chem. Ges.* xvii. 2634.

[6] Morley and Abel, *Ann. Chem. Pharm.* cxl. 347.

Diparatolylamine, $(C_6H_4.CH_3)_2NH$, is obtained by heating paratoluidine with its hydrochloride to 210°—240°. It forms long needles melting at 79°,[1] boils at 355°—360°, and is coloured yellow by nitric acid. Its salts are decomposed by water.

Diparatolylnitrosamine, $(C_6H_4.CH_3)_2N(NO)$, is deposited from petroleum-ether in golden-yellow, hollow, rhombic crystals, melting at 100°—101°. When it is gradually added to well-cooled fuming nitric acid, *hexnitrodiparatolylamine*, $(C_6H(NO_2)_3CH_3)_2NH$, is formed; this crystallizes in small yellow pyramids which melt at 258°, and are slightly soluble in the usual solvents.[2]

Acetparatoluide, $C_6H_4(CH_3)N(C_2H_3O)H$, was first observed by Riche and Bérard in the preparation of aniline oil by means of iron and acetic acid, and then prepared by repeated distillation of paratoluidine with acetic acid.[3] Arndt and Städeler obtained it in the same way from crude aniline, and separated it from the acetanilide formed by dissolving the mixture in acetic acid and precipitating the less soluble acettoluide with water.[4]

Acetparatoluide is dimorphous; on the gradual evaporation of its alcoholic solution it separates in monoclinic crystals; when a hot solution is allowed to cool, however, it crystallizes in rhombic needles.[5] It melts at 147°[6], and boils at 307°.[7] 1,000 parts of water dissolve 0·56 parts at 65°, and 0·886 parts at 22°.

Paratolyl carbamide, $(C_7H_7)NH.CO.NH_2$. Sell prepared this compound by the action of potassium cyanate on toluidine sulphate,[8] and Steiner obtained it, together with ditolylguanidine, by treating fulminate of mercury with paratoluidine.[9] It is readily soluble in hot water, and crystallizes in thick needles melting at 172°.[10]

Diparatolyl carbamide, $(C_7H_7NH)_2CO$, is formed on the distillation of the compound just described (Sell), or when it is heated to 150°—170° with paratoluidine.[11] It is also obtained when carbonyl chloride is passed into a solution of paratoluidine in chloroform.[12] It is insoluble in water, and crystallizes from hot alcohol in flat needles, which resemble those of benzoic acid and melt at 256.°

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[1] *Ber. Deutsch. Chem. Ges.* vi. 446.

[2] Cosack, *ibid.* xiii. 1092; Lehne, *ibid.* xiii. 1544.

[3] *Ann. Chem. Pharm.* cxxix. 77.

[4] *Chem. Centralbl.* 1864, 707.

[5] Panebianco, *Jahresber.* 1878, 678.

[6] Hübner, and Wallach, *Ann. Chem. Pharm.* cliv. 302.

[7] Beilstein and Kuhlberg, *ibid.* clvi. 74.

[8] Beilstein and Kuhlberg, *ibid.* cxxvi. 157.

[9] *Ber. Deutsch. Chem. Ges.* viii. 519.

[10] Cosack, *ibid.* xii. 1450.

[11] Weith, *ibid.* ix. 821.

[12] Michler, *ibid.* ix. 710

Paratolyl urethane, or *Ethyltolyl carbamate*, $(C_7H_7)NH(CO)(OC_2H_5)$, is obtained by the action of chlorocarbonic ether on paratoluidine in ethereal solution. It is insoluble in water and crystallizes from alcohol in long prisms, melting at 52°.

Paratolyl carbimide, $CO.N.C_7H_7$, is obtained by the distillation of the carbamic ether with phosphorus pentoxide, as a strongly refractive liquid boiling at 185°; its vapour possesses a penetrating odour and causes a flow of tears.[1]

Paratolyl thiocarbamide, $(C_7H_7)NH(CS)NH$, is formed when paratoluidine hydrochloride is heated with ammonium thiocyanate,[2] and by the combination of paratolyl mustard oil with ammonia.[3] It is slightly soluble in cold water and crystallizes from hot alcohol in small tablets or thick needles melting at 182°.

Diparatolyl thiocarbamide, $(C_7H_7.NH)_2CS$, crystallizes from hot water in large, pointed prisms, melting at 176°.[4]

Paratolyl thiocarbimide, or *Paratolyl mustard oil*, $CS.N.C_7H_7$. Hofmann obtained this compound by heating the substance just described with phosphorus pentoxide.[5] In order to prepare it, paratolyl thiocarbamide is heated to 160° with 30 per cent. sulphuric acid.[6] It crystallizes from ether in long, white needles, melts at 26°, and boils at 237°. While both its isomerides possess the characteristic pungent odour of the mustard oils, the smell of paratolyl thiocarbimide resembles that of oil of aniseed.

Like other thiocarbimides it combines with ammonia, the amines, and the aromatic amido-bases to form compound thio-ureas.

HALOGEN SUBSTITUTION PRODUCTS OF THE TOLUIDINES.

2050 A very large number of these has been prepared, but only the mono-substitution products will be here described.

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[1] Hofmann, *Ber. Deutsch. Chem. Ges.* iii. 656.
[2] Clermont and Wehrlin, *Bull. Soc. Chim.* xxvi. 126.
[3] Staats, *Ber. Deutsch. Chem. Ges.* xiii. 136.
[4] Sell, *loc. cit.*; Maly, *Jahresber.* 1869, 637.
[5] *Ber. Deutsch. Chem. Ges.* i. 173.
[6] Liebermann and Natanson, *Liebig's Ann.* ccvii. 160.

CHLOROTOLUIDINES, $C_6H_3Cl(CH_3)NH_2$.

CH_3 :	NH_2 :	Cl		Melting-point.	Boiling-point.
1	2	4	small plates[1]	29·5°	241°
1	3	4	thin plates[2]	30°	230°
1	4	3	liquid[3]	—	222°
1	4	2	crystals[4]	26°	237°—238·5°

BROMOTOLUIDINES, $C_6H_3Br(CH_3)NH_2$.

CH_3 :	NH_2 :	Br			
1	2	3	liquid[5]	—	—
1	2	4	plates[6]	32°	253°—257°
1	2	5	rhombohedra[7]	58°	240°
1	3	4	prisms[8]	32°	—
1	3	5	„ [9]	36°	255°—260°
1	3	6	„ [10]	78·5°	240°
1	4	2	„ [11]	26°	—
1	4	3	„ [12]	8°	240°

Neville and Winther have also prepared dibromotoluidines together with higher substitution-products, by methods which give a knowledge of their constitutions.[13]

IODOTOLUIDINES, $C_6H_3I(CH_3)NH_2$.

CH_3 :	NH_2 :	I			
1	2	4	needles[14]	49°	—
1	3	4	small plates[15]	189°	—

[1] Beilstein and Kuhlberg, *Ann. Chem. Pharm.* clvi. 81; clviii. 337.

[2] Gattermann and Kaiser, *Ber. Deutsch. Chem. Ges.* xviii. 2599.

[3] Wroblevsky, *Ann. Chem. Pharm.* clxviii. 153; *Ber. Deutsch. Chem. Ges.* vii. 1062.

[4] Lellmann, *ibid.* xvii. 534.

[5] Neville and Winther, *ibid.* xiii. 1945.

[6] Körner, *Zeitschr. Chem.* 1869, 636; Hübner and Wallach, *Ann. Chem. Pharm.* cliv. 298; Heynemann, *ibid.* clviii. 340; Hübner and Roos, *Ber. Deutsch. Chem. Ges.* vi. 799.

[7] Wroblevsky; Grete, *Ann. Chem. Pharm.* clxxvii. 249.

[8] Neville and Winther, *Ber. Deutsch. Chem. Ges.* xiii. 972.

[9] Wroblevsky, *Ann. Chem. Pharm.* cxcii. 192, 203; Neville and Winther.

[10] Wroblevsky; Neville and Winther.

[11] Neville and Winther, *Ber. Deutsch. Chem. Ges.* xiv. 418.

[12] Wroblevsky, *Ann. Chem. Pharm.* clxviii. 153.

[13] *Ber. Deutsch. Chem. Ges.* xiv. 419.

[14] Heynemann, *loc. cit.*

[15] Glassner, *ibid.* viii. 561.

NITROTOLUIDINES, $C_6H_3(CH_3)NH_2(NO_2)$.

2051 The numbers subjoined refer to the positions of the side-chains in the order given in the formula.

α-Orthonitro-orthotoluidine (1 : 2 : 6) is formed by the partial reduction of the orthodinitrotoluene melting at 60° – 61°. It is slightly soluble in water, more readily in alcohol, and crystallizes in long, light yellow needles melting at 90° – 91°; it may be converted into orthonitrotoluene by the elimination of the amido-group.[1]

β-Orthonitro-orthotoluidine (1 : 2 : 3) is obtained as a by-product in the preparation of the compound next described, and crystallizes from dilute alcohol in orange-yellow prisms, united in bushy aggregates, which melt at 97°. It is converted into metanitrotoluene when heated with a solution of nitrogen trioxide.[2]

Metanitro-orthotoluidine (1 : 2 : 5) is obtained by the nitration of acetorthotoluide and decomposition of the products with the calculated quantity of alcoholic potash. It is readily soluble in alcohol, but only very slightly in boiling water, from which it crystallizes in small, citron-yellow needles, melting at 127° – 128°. On heating with an alcoholic solution of nitrogen trioxide, metanitrotoluene is obtained, while when the amido-group is replaced by bromine, orthobromometanitrotoluene is formed, and can be converted into orthobromotoluene by means of the diazo-reaction.

Paranitro-orthotoluidine (1 : 2 : 4). When the phthalyltoluide obtained by heating orthotoluidine with phthalic anhydride is nitrated, two mononitro-compounds are formed, one of which occurs only in small quantities and on decomposition with ammonia yields the orthonitro-orthotoluidine just described, while the other gives paranitro-orthotoluidine, which melts at 109°, and may be converted into paranitrotoluene by means of the diazo-reaction (Städel). It is also formed when orthotoluidine is dissolved in 10 parts of sulphuric acid and the well-cooled solution treated with the calculated quantity of nitric acid, mixed with twice its weight of sulphuric acid. The

[1] Cunerth, *Ann. Chem. Pharm.* clxxii. 223; Bernthsen, *Ber. Deutsch. Chem. Ges.* xv. 3016; Städel, *Ann. Chem. Pharm.* ccxxv. 384.

[2] Lellmann and Würthner, *ibid.* ccxxviii. 239.

[3] Beilstein and Kuhlberg, *ibid.* clviii. 345.

corresponding nitracet-toluide is obtained in a similar manner by dissolving acetorthotoluide in 20 parts of sulphuric acid; if, however, only 4 parts be taken, the acetyl-compound of metanitro-orthotoluidine is also formed.[1]

a-Orthonitrometatoluidine (1 : 3 : 2) is prepared by the nitration of acetmetatoluide and decomposition of the product with alcoholic potash. It crystallizes in fine, saffron-yellow needles melting at 132°—134°. On heating with an alcoholic solution of nitrogen trioxide, it is converted into orthonitrotoluene (Beilstein and Kuhlberg).

β-Orthonitrometatoluidine (1 : 5 : 2) was obtained by Limpricht from the corresponding dinitrotoluene (p. 71). It is slightly, soluble in cold, more readily in hot water, and readily in alcohol; crystallizes in reddish yellow needles, and may be converted into orthonitrotoluene by means of the diazo-reaction.[2]

Orthonitroparatoluidine (1 : 4 : 2) was obtained by the partial reduction of ordinary dinitrotoluene.[3] This compound alone is formed when the reduction is effected with ammonium sulphide in the cold; if, however, the mixture be warmed, paranitro-orthotoluidine is also formed.[4] Orthonitroparatoluidine is best prepared by dissolving 100 grams. of paratoluidine in 2,000 grams. of concentrated sulphuric acid, and gradually adding a mixture of 75 grams. of concentrated nitric acid with 300 grams. of sulphuric acid to the solution cooled below 0°. After standing for some time, the liquid is poured into ice-water.[5] It crystallizes from hot water in broad, yellow, monoclinic needles (Panebianco), melting at 77·5°, and may be converted into orthonitrotoluene by means of the diazo-reaction.

Metanitroparatoluidine (1 : 4 : 3) was obtained by Beilstein and Kuhlberg from acetnitroparatoluide; the latter is best prepared by dissolving acetparatoluide in 4 parts of sulphuric acid, and adding the calculated amount of nitric acid mixed with 2 parts of sulphuric acid to the well-cooled solution. If the amount of sulphuric acid be increased, the acetyl-compound of orthonitroparatoluidine is also formed, while metanitroparatoluidine can be obtained by the direct nitration of paratoluidine if less sulphuric acid be used (Nölting and Collin).

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[1] Nölting and Collin, *Ber. Deutsch. Chem. Ges.* xvii. 261.

[2] *Ibid.* xviii. 1401.

[3] Beilstein and Kuhlberg, *Ann. Chem. Pharm.* clv. 14.

[4] Limpricht, *Ber. Deutsch. Chem. Ges.* xviii. 1400; Graeff, *Ann. Chem. Pharm.* ccxxix. 340.

[5] Nölting and Collin, *loc. cit.*

It is readily soluble in alcohol, but only slightly in boiling water, and crystallizes in red needles or prisms, melting at 116°.[1] On heating with a solution of ethyl nitrite, metanitrotoluene is formed.

Metanitroparamethyltoluidine, $C_6H_3(NO_2)(CH_3)NH(CH_3)$, is obtained by heating nitrotoluidine with methyl iodide and wood-spirit; it crystallizes from alcohol in red needles, and from benzene in tablets melting at 84°—85°.

Metanitropara-ethyltoluidine, $C_6H_3(NO_2)(CH_3)NH(C_2H_5)$, forms large, red needles melting at 58°—59° (Gattermann).

DINITROTOLUIDINES, $C_6H_2(CH_3)(NO_2)_2NH_2$.

2052. *a-Dinitro-orthotoluidine* (1 : 3 : 5 : 2) is formed when dinitro-orthocresyl ethyl ether is heated with alcoholic ammonia. It is scarcely soluble in boiling alcohol, slightly in toluene, and crystallizes in prisms or tablets which exhibit a blue iridescence and melt at 208°.[2]

β-Dinitrotoluidine is obtained by heating β-trinitrotoluene with alcoholic ammonia; it crystallizes from glacial acetic acid in short, golden-yellow needles, melting at 94°.

γ-Dinitrotoluidine is formed, even in the cold, by the action of alcoholic ammonia on γ-trinitrotoluene; it is almost insoluble in the ordinary solvents with the exception of hot acetone and glacial acetic acid, and forms small, hard, golden-yellow crystals melting at 192°—193°.

Adjacent Dinitroparatoluidine (1 : 3 : 5 : 4) is formed when acetparatoluide is brought into concentrated nitric acid and the product treated with alcoholic potash;[3] it may also be obtained by the action of alcoholic potash on dinitroparacresyl ethyl ether.[4] It is slightly soluble in alcohol, and crystallizes from carbon disulphide in yellow needles, melting at 168°.[5] Chromic acid oxidizes it to chrysanisic acid, $C_6H_2(CO_2H)(NO_2)_2NH_2$.

Symmetric Dinitroparatoluidine (1 : 2 : 6 : 4) is obtained by the reduction of *a*-trinitrotoluene with ammonium sulphide; it crystallizes from acetic acid in yellow, hair-like needles, melting at 166·5°—168°. It does not yield chrysanisic acid on oxidation, but a brown powder which is probably an azo-compound.[1]

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[1] Gattermann, *Ber. Deutsch. Chem. Ges.* xviii. 1482

[2] Städel, *ibid.* xiv. 900.

[3] Beilstein and Kuhlberg, *Ann. Chem. Pharm.* clviii. 341; Kelbe, *Ber. Deutsch. Chem. Ges.* viii. 877.

[4] Städel, *loc. cit.*

[5] Hübner, *Ann. Chem. Pharm.* ccxxii. 74.

Thiotoluidine, $(CH_3.C_6H_3.NH_2)_2S$, is formed when paratoluidine is heated with sulphur and litharge to 140°. It crystallizes from alcohol in lustrous, odourless plates melting at 103°, and is a di-acid base. Its salts crystallize well, but are decomposed by a large quantity of water. When the solution is heated with ferric chloride or any other oxidizing agent, it first becomes yellow, passing into brownish red, and then to dull red, a dark flocculent precipitate being finally formed.[2]

DIAMIDOTOLUENES, or TOLYLENEDIAMINES,
$C_6H_3(CH_3)(NH_2)_2$.

2053 *a-Diamidotoluene*, or *ordinary Metatoluylenediamine* (1:2:4) was discovered by Hofmann in the high boiling portions of crude aniline oil,[3] and was then obtained by him as a product of the reduction of ordinary dinitrotoluene with iron and acetic acid. It is best prepared by the reduction of dinitrotoluene with tin and hydrochloric acid.[4] It crystallizes from hot water in long needles, melts at 99°, and boils at about 280°. Its aqueous solution becomes dark-coloured in the air.

a-Diamidotoluene monohydrochloride, $C_7H_{10}N_2.HCl$, is obtained by dissolving the base in the calculated amount of hydrochloric acid, and is left as a radiating crystalline mass when the solution is evaporated.[5]

a-Diamidotoluene dihydrochloride, $C_7H_{10}N_2(ClH)_2$, crystallizes from warm hydrochloric acid in needles.

a-Diamidotoluene sulphate, $C_7H_{10}N_2.SO_4H_2 + 2H_2O$, crystallizes from water in long prisms, with a vitreous lustre, and is precipitated in crystals by the addition of alcohol to its aqueous solution.

β-Diamidotoluene, or *Orthotoluylenediamine* (1 : 3 : 4) is formed by the reduction of metanitroparatoluidine with tin and hydrochloric acid. It forms brilliant white scales, which are tolerably stable when dry; its aqueous solution, on the contrary, rapidly becomes coloured black in the air. It melts at 88·5°, and boils at 265°.

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[1] Beilstein, *Ber. Deutsch. Chem. Ges.* xiii. 243.

[2] Merz and Weith, *ibid.* iv. 393.

[3] *Jahresb. Chem.* 1861, 512; Hell and Schoop, *Ber. Deutsch. Chem. Ges.* xii. 723.

[4] Beilstein, *Ann. Chem. Pharm.* cxxx. 242.

[5] Bernthsen, *Ber. Deutsch. Chem. Ges.* xi. 1759.

When a crystal is thrown into water it takes up a rapid rotatory motion in dissolving, as do the other diamines (Pt. III. p. 238).

β-Diamidotoluene hydrochloride, $C_7H_{10}N_2(ClH)_2$, crystallizes in long, very soluble needles.

β-Diamidotoluene sulphate, $2(C_7H_{10}N_2SO_4H_2) + 3H_2O$, is more readily soluble in water than the *a*-compound, and is precipitated by alcohol in brilliant white scales, with a nacreous lustre.[1]

Methyl-β-diamidotoluene, or *Metamidoparamethyltoluidine*, $C_6H_3(CH_3)(NH_2)NH(CH_3)$, is prepared in a similar manner to the following compound, and crystallizes in four-sided tablets, melting at 43°—44°.

Ethyl-β-diamidotoluene, $C_6H_3(CH_3)(NH_2)NH(C_2H_5)$, is obtained by the reduction of metanitropara-ethyltoluidine, and crystallizes from sulphuretted hydrogen water in large, colourless tablets, which melt at 54°—55°, and soon become dark-coloured in the air. The peculiar rotatory motion assumed by the diamines when dissolving in water was first observed with this compound. A crystal which is not too heavy acquires such a rapid motion that it appears to have a completely closed path. A trace of fat on the water causes cessation of the motion (Gattermann).

γ-Diamidotoluene, or *Paratoluylenediamine* (1 : 3 : 5) was obtained by Beilstein and Kuhlberg from metanitro-orthotoluidine; it is also formed when ortho-amido-azotoluene or metamido-azotoluene is reduced with tin and hydrochloric acid.[2] It is readily soluble in water, crystallizes from hot benzene in aggregates of tablets, melts at 64°, and boils at 273°—274°. On oxidation with manganese dioxide and sulphuric acid, it yields toluquinone.

γ-Diamidotoluene hydrochloride, $C_7H_{10}N_2(HCl)_2$, crystallizes from hot hydrochloric acid in small plates with a nacreous lustre.

γ-Diamidotoluene sulphate, $C_7H_{10}N_2.SO_4H_2$, is slightly soluble in cold, more readily in hot water, and is precipitated from this solution by alcohol as a white powder.

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[1] Beilstein and Kuhlberg, *Ann. Chem. Pharm.* clviii. 351.

[2] Nietzki, *Ber. Deutsch. Chem. Ges.* x. 832, 1158.

As already mentioned, solutions of its salts to which a little orthotoluidine has been added are coloured a deep green by ferric chloride. Nietzki at first attributed the colouration to paratoluylene-diamine alone, but he afterwards found that the colour was only produced in samples prepared from ortho-amido-azotoluene, which had not been completely freed from orthotoluidine; the pure compound only gives the reaction after the addition of the latter base.

δ-*Diamidotoluene* (1 : 2 : 3) is formed by the reduction of β-orthonitro-orthotoluidine. It forms red crystals, which are readily taken up by the usual solvents, smell like acetamide, melt at 61°—62° and boil at 255°.[1]

DIAZO-DERIVATIVES OF TOLUENE.

2054. Only the derivatives of paratoluidine have hitherto been prepared pure; they are obtained by the methods used in the preparation of the corresponding benzene derivatives.[2]

The diazo-compounds of the two other toluidines have only been obtained as intermediate products in the preparation of derivatives; many examples of this kind have already been given.

Diazotoluene nitrate, $CH_3.C_6H_4N{=}NO.NO_2$, crystallizes in white needles.

Diazotoluene sulphate, $CH_3.C_6H_4N{=}N.O.SO_2.OH$, forms lustrous needles or prisms.

Diazo-amidotoluene, $CH_3.C_6H_4N{=}N.NH.C_6H_4.CH_3$, is prepared by passing nitrogen trioxide into a solution of paratoluidine in a mixture of alcohol and ether.[3] It crystallizes in yellow or reddish yellow needles or prisms, and gives a platinichloride $(C_{14}H_{16}N_3)_2PtCl_6$, which forms yellow tablets.

Diazobenzene-amidotoluene, $C_6H_5N_2.NH.C_6H_4.CH_3$, was obtained by Griess as a product of the action of diazobenzene nitrate on paratoluidine,[4] as well as of that of diazotoluene nitrate on aniline.[5] It crystallizes in narrow, yellow plates. The formation of the same compound by two different reactions which should yield isomeric substances, is analogous to the case of diazobromobenzene-amidobenzene, which has been already discussed.

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[1] Lellmann and Würthner, *Ann. Chem. Pharm.* ccxxviii. 243.

[2] Griess, *Jahresb. Chem.* 1866, 458.

[3] Griess, *Ann. Chem. Pharm.* cxxi. 277

[4] *Ibid.* cxxxvii. 60.

[5] *Ber. Deutsch. Chem. Ges.* vii. 1619.

HYDRAZINE-DERIVATIVES OF TOLUENE.

2055 *Paratolylhydrazine*, $CH_3.C_6H_4.NH{=}NH_2$, is prepared from paratoluidine just as is phenylhydrazine from aniline. It crystallizes from ethereal solution in rhombic tablets, melts at 61°, boils with slight decomposition between 240°—244°, and is slightly soluble in water, but readily in alcohol.[1]

Diparatolylhydrazine, $(CH_3.C_6H_4)_2N{=}NH_2$, is formed by the action of zinc-dust and acetic acid on diparatolylnitrosamine; it crystallizes from benzene in colourless plates melting at 171°—172°, and is a weak monacid base. Mercuric oxide converts it into diparatolylamine without the formation of a tetrazone-compound (Pt. III. p. 29).[2]

AZO-DERIVATIVES OF TOLUENE.

2056 *Azotoluenes*, $CH_3.C_6H_4N{=}NC_6H_4.CH_3$, are formed by reduction of the nitrotoluenes or oxidation of the toluidines, and are converted into hydrazotoluenes, $C_7H_7.NH-NH.C_7H_7$, by further reduction.

Ortho-azotoluene is obtained by the action of zinc-dust and alcoholic potash, or sodium amalgam and alcohol on orthonitrotoluene,[3] as well as by the oxidation of orthotoluidine with potassium permanganate, ammonia and oxalic acid being simultaneously formed.[4] It is volatile with steam and crystallizes from ether in red prisms melting at 55°. It is reduced to *orthohydroazotoluene* by the further action of sodium amalgam; this forms colourless crystals melting at 165°, which decompose at a higher temperature into orthotoluidine and ortho-azotoluene, and are readily oxidized to the latter in the air.

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[1] E. Fischer, *Ber. Deutsch. Chem. Ges.* ix. 890.

[2] Lehne, *ibid.* xiii. 1546.

[3] Petriew, Beilstein's *Org. Chem.* 976; *Ber. Deutsch. Chem. Ges.* vi. 557.

[4] Hoogewerff and van Dorp, *ibid.* xi. 1203.

Meta-azotoluene is most readily formed by treating metanitrotoluene with zinc-dust and alcoholic potash.[1] It crystallizes from weak alcohol in orange-coloured rhombic prisms melting at 55°. When it is heated with alcoholic ammonium sulphide, the liquid *metahydrazotoluene* is formed and rapidly re-oxidizes in the air.

Para-azotoluene may be best obtained by dissolving 1 part of paranitrotoluene in 10 parts of alcohol and gradually adding 22 parts of 4 per cent. sodium amalgam together with a sufficient quantity of acetic acid.[2] The oxidation of paratoluidine with potassium permanganate affords a very poor yield of the azo-compound, but better results may be obtained by oxidizing the sulphate of the base with potassium ferricyanide (Barsilowsky). It is also formed by the action of chromic acid on a solution of paratoluidine in glacial acetic acid,[3] and by that of bleaching powder on the base dissolved in chloroform.[4]

It is slightly soluble in alcohol, readily in ether and petroleum-spirit, crystallizing from the latter in orange-yellow needles which melt at 144°. When it is heated to 100° with alcoholic ammonia in a closed vessel, *parahydrazotoluene* is formed and crystallizes in large needles or tablets which melt at 124° and decompose into paratoluidine and parazotoluene when more strongly heated. It rapidly becomes oxidized to the latter when its alcoholic solution is exposed to the air (Melms).

Barsilowsky, by the oxidation of paratoluidine with potassium ferricyanide, obtained parazotoluene and an isomeric substance,[5] which Perkin also obtained by the action of potassium dichromate on a solution of toluidine sulphate.[6] It forms red, hexagonal crystals and is a weak base; Perkin was only able to prepare its platinichloride, from the composition of which he concluded that the compound was a triparatolylenediamine, $C_{21}H_{21}N_3$, while Barsilowsky found that it is reduced by alcoholic ammonium sulphide to a compound isomeric with hydrazotoluene, which crystallizes in small colourless plates and readily oxidizes in the air. It is a weak base and forms a very characteristic oxalate, $(C_{14}H_{16}N_2)_2C_2H_2O_4 + H_2O$, which separates from dilute alcohol in star-like aggregates, which are very similar to the seed feathers of the dandelion.

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[1] Barsilowsky, *Ann. Chem. Pharm.* ccvii. 114.
[2] Helms, *Ber. Deutsch. Chem. Ges.* iii. 549.
[3] Perkin, *Journ. Chem. Soc.* 1880, i. 553.
[4] Schmitt, *Journ. Prakt. Chem.* [2] xviii. 198.
[5] *Ann. Chem. Pharm.* ccvii. 102.
[6] *Journ. Chem. Soc.* 1880, i. 546.

Klinger and Pitschke have now found that the red substance is an amido-azo-compound of the formula $C_{28}H_{28}N_4$.[1] It is decomposed into paratoluidine and *paraleucotoluidine*, $C_{21}H_{23}N_3$, by energetic reduction with tin and hydrochloric acid. This compound crystallizes in small colourless plates and is readily oxidized to *pararosotoluidine*, $C_{21}H_{21}N_3$, which forms small lustrous red plates, and dissolves in water with an intense violet-red colour. The red substance has, therefore, the following constitution, $C_{21}H_{17}(NH_2)_2N = N.C_6H_4.CH_3$. These compounds will be more fully described in the sequel.

Ortho-azoxytoluene, $C_{14}H_{14}N_2O$, is formed when orthonitrotoluene is heated with a solution of sodium in methyl alcohol and crystallizes from warm petroleum-ether in yellow, monoclinic needles melting at 59°—60°. It is not converted into the isomeric hydroxyazotoluene, $C_7H_7.N_2.C_7H_6.OH$, on heating with concentrated sulphuric acid, but a large quantity of orthotoluidine is formed, the oxygen thus liberated producing the oxidation of a portion of the ortho-azoxytoluene to a mixture of amorphous acids.

Klinger and Pitschke consider that the conversion of azoxybenzene into hydroxyazobenzene (Pt. III. p. 297) is brought about in a similar manner, and may be looked upon as "hydroxylation by direct oxidation."[2]

Amido-azotoluenes, $CH_3.C_6H_4.N = N.C_6H_3(CH_3)NH_2$, are formed by the action of nitrous acid on orthotoluidine and metatoluidine, while paratoluidine, as already mentioned, is thus converted into diazo-amidotoluene. Compounds belonging to this group are also formed by the action of a diazoparatoluene salt on orthotoluidine or metatoluidine, as well as on aniline, etc.[3]

Amidortho-azotoluene is obtained by passing nitrogen trioxide into orthotoluidine floating on a saturated solution of common salt. The product is allowed to stand for some time, washed with water to remove any orthocresol which has been formed, treated with dilute caustic soda and finally boiled with dilute hydrochloric acid, the hydrochloride thus obtained being then decomposed by ammonia.

Amidortho-azotoluene is slightly soluble in water, readily in alcohol, and crystallizes in lustrous, golden plates or tablets, melting at 100°. The hydrochloride, $C_{14}H_{15}N_3.ClH$, is only slightly soluble in water, and crystallizes in long, thin tablets with a silver lustre.

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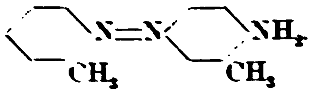
[1] *Ber. Deutsch. Chem. Ges.* xvii. 2439.
[2] *Ibid.* xviii. 2551.
[3] Nietzki, *ibid.* x. 662, 832, 1156.

This compound is decomposed into orthotoluidine and paratolylenediamine by the action of hydrochloric acid and tin or zinc dust, and has therefore the following constitution:



Amidometa-azotoluene crystallizes from alcohol in broad, golden-yellow needles melting at 80°. The hydrochloride forms long, dark blue needles, which are only slightly soluble in hot alcohol, and, like all the other salts of this class, is decomposed by water. On reduction with tin and hydrochloric acid, paratolylenediamine is formed.

Ortho-amidopara-azotoluene forms yellow tablets melting at 127°—128°; its hydrochloride crystallizes in cinnabar-red needles, which appear of a steel-blue colour when seen by reflected light.

Metamidoparazotoluene crystallizes from alcohol in large, yellow, plates, melting at 127°; the hydrochloride forms small, steel-blue needles.

Para-amidopara-azotoluene. In order to prepare this compound, the isomeric diazo-amidoparatoluene is heated for twelve hours to 65° with five times its weight of paratoluidine and one equivalent of paratoluidine hydrochloride. It crystallizes from alcohol or acetic ether, in orange-red lustrous needles melting at 118·5°. Its hydrochloride crystallizes in light yellow needles and forms a green solution in water. It is converted into paratoluidine and orthotolylenediamine by reduction.[1]

On treatment with fuming sulphuric acid, a mixture of disulphonic acids is formed, which comes into the market as "Acid yellow R," since it dyes a redder shade than the colouring matter obtained from amido-azobenzene (Part III. p. 307), which is therefore called "Acid yellow G."

a-Azoxytoluidine, $C_{14}H_{12}N_2(NH_2)_2O$, is formed by the action of sodium amalgam on a solution of orthonitroparatoluidine in absolute alcohol, and crystallizes from hot water in small, yellow needles melting at 148°. It is a diacid base, and on further reduction yields the following compounds:

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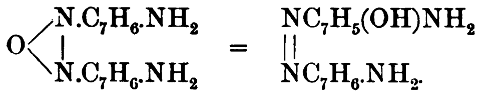
[1] Nolting and Witt, *Ber. Deutsch. Chem. Ges.* xvii. 77.

a-Azotoluidine, or *Symmetric a-diamido-azotoluene*, $C_{14}H_{12}N_2(NH_2)_2$, crystallizes from hot water in red needles which are readily soluble in alcohol and melt at 159°.

a-Hydrazotoluidine, $C_{14}H_{12}(N_2H_2)(NH_2)_2$, is almost insoluble in cold water and alcohol, but is slightly soluble in hot alcohol; it forms small, colourless, rhombic tablets which melt at 180°. It is tolerably stable in contact with cold water and alcohol, but rapidly oxidizes when heated with them in the air.[1]

β-Azoxytoluidine, $C_{14}H_{12}N_2(NH_2)_2O$, is obtained from paranitro-orthotoluidine and crystallizes in long, yellow to yellowish red, silky needles melting at 168°; its salts crystallize well. When heated with concentrated sulphuric acid, it is converted into the isomeric hydroxyazo-compound, just as is the case with azoxybenzene (Part III. p. 296):



$$O\left\langle\begin{matrix}N.C_7H_6.NH_2\\ |\\ N.C_7H_6.NH_2\end{matrix}\right. = \begin{matrix}NC_7H_5(OH)NH_2\\ \|\\ NC_7H_6.NH_2.\end{matrix}$$

This compound crystallizes from alcohol in small, dark red needles, which melt at 212° with decomposition. Its hydrochloride and sulphate are only slightly soluble in water. On treatment with stannous chloride and hydrochloric acid, it is resolved into ordinary diamidotoluene and *diamidocresol*, $C_6H_2(CH_3)(NH_2)_2OH$, the hydrochloride of which crystallizes in white needles which become coloured blue in the air; the free base immediately becomes resinous.

β-Azotoluidine, or *Symmetric β-diamido-azotoluene*, $C_{14}H_{12}N_2(NH_2)_2$, crystallizes from hot water in small, yellow needles, and is deposited on the gradual evaporation of its alcoholic solution in long, red needles, which melt at 197°, and are slightly soluble in water, readily in alcohol. The sulphate is only slightly soluble in water, the hydrochloride being somewhat more readily dissolved.

β-Hydrazotoluidine, $C_{14}H_{12}(N_2H_2)(NH_2)_2$, forms yellow needles which rapidly oxidize when exposed to the air in a moist state. It decomposes without melting when heated, and burns with a brilliant flame. It is almost insoluble in absolute alcohol, but dissolves readily in dilute alcohol and water.[2]

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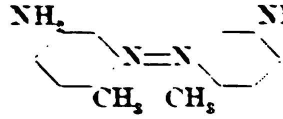
[1] Buckney, *ibid.* xi. 1451.

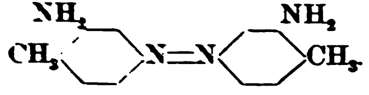
[2] Limpricht, *Ber. Deutsch. Chem. Ges.* xviii. 1403; Graff, *Ann. Chem. Pharm.* ccxxix. 340.

The constitutions of the two azotoluidines are expressed by the following formulæ:

α.



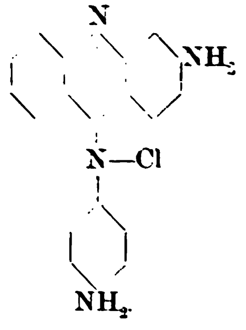
β.



Metanitroparatoluidine is immediately converted by sodium amalgam into the corresponding diamidotoluene, while metanitro-ortho- and *a*-orthonitrometa-toluidine yield resinous products on oxidation (Limpricht).

Asymmetric diamido-azotoluene, $C_7H_7N{=}NC_7H_5(NH_2)_2$, corresponds to chrysoïdine (Part III. p. 301) and is formed by the action of diazotoluene nitrate on *a*-diamidotoluene. It crystallizes from alcohol in orange-yellow needles melting at 183°. Its hydrochloride, $(C_{14}H_{16}N_4)ClH$, forms red needles.[1]

2057 *Tolusafranine*, $C_{21}H_{20}N_4$. The history of this dye, which is simply known as "safranine" in commerce, has already been briefly indicated. Phenosafranine chloride, the lower homologue of tolusafranine, has been proved[2] to have the following constitution:



This formula explains all the facts which have been already given (Part III. p. 369) concerning this substance, and also its formation from one molecule of paradiamidobenzene and two molecules of aniline.

Hofmann and Geyger were the first to subject the commercial product to a searching examination; they ascertained that it is a hydrochloride of the formula $C_{21}H_{21}N_4Cl$, which is not attacked by alkalis, but is readily decomposed by moist silver oxide, and that it is not a derivative of aniline, as had been up to that time assumed, but of orthotoluidine, from which it can be obtained by the action of nitrous acid and oxidation of the products with arsenic or chromic acids.[1] Witt then found that it is formed by heating amido-ortho-azotoluene with orthotoluidine hydrochloride,[2] and by the oxidation of a mixture of orthotoluidine and paratoluylenediamine.[3] In order to prepare it, a solution of equal molecules of orthotoluidine and hydrochloric acid is treated with the calculated quantity of sodium nitrate, to obtain amido-ortho-azotoluene; the product, after the addition of some orthotoluidine hydrochloride, is allowed to stand and is then reduced with zinc-dust and hydrochloric acid, a mixture of γ-diamidotoluene and orthotoluidine being formed, which is then neutralized and oxidized with potassium dichromate; if the solution were kept acid, toluquinone would be formed.[4] The safranine is then precipitated with common salt, filtered off, pressed, dried and brought into the market.[5]

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[1] Hofmann, *Ann. Chem. Pharm.* x. 218.

[2] Witt, *Ber. Deutsch. Chem. Ges.* xix. 3121. Nietzki, *ibid.* 3163.

Tolusafranine hydrochloride, $C_{21}H_{21}N_4Cl$, is tolerably soluble in water and alcohol, forming red solutions which possess a characteristic fluorescence; the salt is precipitated from its aqueous solution by the addition of hydrochloric acid in red crystals, which are best obtained by crystallizing the commercial product from boiling, dilute alcohol. The free base, obtained from this compound by means of silver oxide, probably has the formula $C_{21}H_{21}N_4OH$, and forms reddish brown crystals which take a faint green metallic lustre on drying, but have not yet been obtained free from silver chloride; they are soluble in water and alcohol, but not in ether.

Tolusafranine nitrate, $C_{21}H_{21}N_4.NO_3$, crystallizes in reddish brown needles which are only very slightly soluble in cold water.

Tolusafranine picrate, $C_{21}H_{20}N_4.C_6H_3(NO_2)_3O$, is obtained by the addition of picric acid to a solution of one of the salts of the base, and forms brownish red needles, insoluble in water, alcohol and ether.

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[1] *Ber. Deutsch. Chem. Ges.* v. 526.
[2] *Ibid.* x. 874.
[3] *Ibid.* xii. 939; Bindschedler, *ibid.* xiii. 207.
[4] Nölting, Schultz, *Steinkohlentheer*, 1049.
[5] *Ibid.* 527.

Tolusafranine shows all the characteristic reactions of the safranines (Part III. p. 323).

It is employed as a substitute for saffron for dyeing silk and cotton mordanted with tannin.

2058 *Toluylene-blue*, $C_{15}H_{18}N_4.HCl + H_2O$, is formed when 36 grms. of nitrosodimethylaniline hydrochloride, and 24 grms. of metatoluylenediamine, each dissolved in 500 c.cm. of water at 30°, are mixed; evolution of heat takes place and a deep green colouration is produced. If the solution be now allowed to stand, flat, lustrous brown prisms separate out, but gradually fall into a fine crystalline powder. These readily form blue solutions in water, alcohol and acetic acid; traces of free mineral acids change the colour into reddish brown, the original shade being restored by alkalis. The base is precipitated by alkalis from its solution as a resinous mass which takes a cupreous lustre in the air.

Toluylene-blue is converted by tin and hydrochloric acid into the leuco-compound, $C_{15}H_{20}N_4HCl$, which is a deliquescent crystalline substance and is very readily re-oxidized.

Toluylene-red, $C_{15}H_{16}N_4$, is formed, together with the leuco-compound, when toluylene-blue is boiled with water for 15-20 minutes. Stannous chloride precipitates the colouring matter as a double tin salt in crystals, which are then decomposed by an alkali.

Toluylene-red crystallizes in orange-red needles containing four molecules of water, which they lose at 150°—160°. The anhydrous base is blood-red and only slightly soluble in alcohol; it forms rose-red normal salts, which are stable and readily soluble in water, while its acid salts are coloured blue and are decomposed by water.

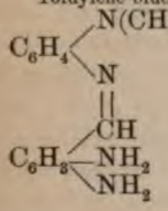
Toluylene-violet, $C_{14}H_{14}N_4$, is formed by warming toluylene-blue with metatoluylenediamine dissolved in dilute acetic acid for twelve hours to 35°—40°, the leuco-base of the blue compound being simultaneously formed:

$$3C_{15}H_{18}N_4 + 2C_7H_{10}N_2 = C_{14}H_{14}N_4 + 3C_{15}H_{20}N_4.$$

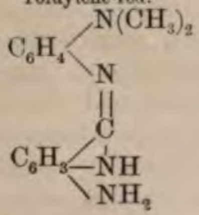
Toluylene-violet forms red crystals with a green reflection and is even less soluble than toluylene-red; its solution is flesh-coloured and shows a remarkable orange-yellow fluorescence. Its slightly soluble normal salts are coloured violet and crystallize well, while the acid salts have a grass-green colour.

Witt gives the following constitutional formulæ for these compounds:[1]

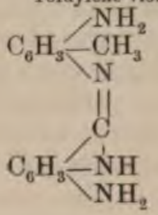
Toluylene-blue.



Toluylene-red.



Toluylene-violet.



PHOSPHORUS DERIVATIVES OF TOLUENE.

2059 *Paratolylphosphorus dichloride*, $CH_3.C_6H_4PCl_2$, is obtained by the continued heating of 15 parts of toluene with 200 parts of phosphorus trichloride and 3 parts of aluminium chloride, or by heating mercury paratolyl with phosphorus trichloride to 180°—190°.[2] It is a crystalline mass, which fumes slightly in the air, melts at 25°, and boils at 245°.

Paratolylphosphorus tetrachloride, $CH_3.C_6H_4PCl_4$, is formed by the combination of the compound just described with chlorine, and crystallizes from benzene in pointed prisms melting at 42°. When heated in a sealed tube to 200°, it decomposes with formation of the dichloride and parachlorobenzyl chloride:

$$2CH_3.C_6H_4PCl_4 = CH_3.C_6H_4PCl_2 + CH_2Cl.C_6H_4Cl + PCl_3 + HCl.$$

It rapidly deliquesces in the air, forming *paratolylphosphorus oxychloride*, $CH_3.C_6H_4POCl_2$, which is, however, best obtained in a similar manner to phenylphosphorus oxychloride, by the action of sulphur dioxide on the tetrachloride. It is a thick liquid, boiling at 284°—285°.

Paratolyl phosphenylous acid, $CH_3.C_6H_4PO_2H_2$, is formed by the action of water on the dichloride. It is slightly soluble in water and crystallizes from alcohol in tablets melting at 104°—105°.

Paratolylphosphenilic acid, $CH_3.C_6H_4PO(OH)_2$, is obtained by decomposing the tetrachloride or the oxychloride with water. It is readily soluble in alcohol and crystallizes from water in matted, woolly needles which melt at 181°. It is decomposed by ignition with lime, with formation of toluene and calcium phosphate. Potassium permanganate oxidizes it to *parabenzophosphenilic acid*, $CO_2H.C_6H_4PO(OH)_2$, which will be described under benzoic acid.

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[1] *Ber. Deutsch. Chem. Ges.* xii. 931.

[2] Michaelis and Paneck, *Liebig's Ann.* ccxii. 203.

Paratolylphosphine, $CH_3.C_6H_4.PH_2$, is obtained by heating tolylphosphenylous acid in an atmosphere of carbon dioxide. It is a liquid which possesses a most intense smell, inhalation of its vapour producing headache and bleeding of the nose. It boils at 178° and solidifies at a lower temperature to a crystalline mass which melts at 4°. It is rapidly oxidized to tolylphosphenylous acid in the air. It combines with hydriodic acid to form *paratolylphosphonium iodide*, $CH_3.C_6H_4.PH_3I$, crystallizing in broad, lustrous needles which deliquesce in the air and sublime in cubes when heated to 340° in a current of carbon dioxide.

Dimethylparatolyl phosphine, $CH_3.C_6H_4.P(CH_3)_2$, is obtained by the action of zinc methyl on the dichloride, and is a liquid which has an unpleasant smell, boils at 210°, dissolves in acids and is not oxidized by exposure to the air. Mercuric oxide converts it into *dimethyltolylphosphine oxide*, $CH_3.C_6H_4.P(CH_3)_2O$, which is a thick liquid. The phosphine combines with methyl iodide to form $CH_3.C_6H_4P(CH_3)I$, crystallizing in needles which melt at 225° and yield a strongly alkaline, deliquescent hydroxide.[1] The corresponding chloride is a very hygroscopic crystalline body.[2]

Orthotolylphosphorus dichloride, $CH_3.C_6H_4PCl_2$, is obtained by heating orthomercury tolyl with phosphorus trichloride. It is a liquid which boils at 244° and does not solidify even at $-20°$. It combines with chlorine forming the tetrachloride as a solid yellow mass. It is decomposed by water with formation of *orthotolylphosphenylous acid*, which is a liquid but forms crystalline salts, while the *orthotolylphosphenilic acid* obtained from the tetrachloride consists of small crystalline grains which melt at 141° (Michaelis and Paneck).

ARSENIC DERIVATIVES OF TOLUENE.

2060 *Arsenparatolyl chloride*, $CH_3.C_6H_4AsCl_2$, is obtained by heating mercury paratolyl with arsenic trichloride.[3] It crystallizes in tablets, melts at 31°, and boils in an atmosphere of carbon dioxide at 267° without decomposition. It combines with chlorine forming the tetrachloride, a yellow crystalline mass, which is semi-fluid at the ordinary temperature but solidifies completely on cooling. It is converted by water into *tolylarsenic acid*, $CH_3.C_6H_4AsO(OH)_2$, which crystallizes in long, thin needles. When the dichloride is boiled with caustic soda solution, *arsentolyl oxide*, $CH_3.C_6H_4AsO$, is formed as a powder melting at 156°.

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[1] Czimatis, *Ber. Deutsch. Chem. Ges.* xv. 2014.

[2] *Ibid.* 2018.

[3] Michaelis and La Coste, *Ann. Chem. Pharm.* cci. 246.

Arsendiparatolyl chloride, $(CH_3.C_6H_4)_2AsCl$, is formed when mercury tolyl is boiled for a long time with three or four times its amount of arsentolyl chloride.[1] It is an oily, yellow liquid which is converted by boiling alcoholic potash into *arsenditolyl oxide* $((CH_3.C_6H_4)_2As)_2O$, which crystallizes from ether in silky needles melting at 98°. The monochloride combines with chlorine to form *arsendiparatolyl trichloride*, $(CH_3.C_6H_4)_2AsCl_3$, a yellow powder which is immediately converted by water into *diparatolylarsenic acid*, $(C_7H_7)_2AsO(OH)$, a white crystalline mass which is slightly soluble in water, readily in alcohol, from which it crystallizes in granules melting at 167°. It is oxidized by an alkaline solution of potassium permanganate to *dibenzoarsenic acid*, $(CO_2H.C_6H_4)_2AsO_2H$.

Triparatolylarsine, $(CH_3.C_6H_4)_3As$, is formed by heating arsenparatolyl oxide to 360°:

$$3CH_3.C_6H_4AsO = (CH_3.C_6H_4)_3As + As_2O_3.$$

It separates from ethereal solution in large crystals which melt at 145° and only volatilize at temperatures above 360°. When chlorine is passed into its chloroform solution, *arsentritolyl dichloride*, $(CH_3.C_6H_4)_3AsCl_2$, is formed as a white crystalline mass which is dissolved almost without decomposition by boiling water.

Tritolylarsine is oxidized by alkaline potassium permanganate solution to *tribenzo-arsenic acid*, $(CO_2H.C_6H_4)_3As(OH)_2$, which will be described under benzoic acid.

Arsenorthotolyl chloride, $C_6H_3.C_6H_4AsCl_2$, has been obtained from mercury orthotolyl and arsenic trichloride, and is a faintly smelling liquid which boils at 264°—265° in an atmosphere of carbon dioxide without undergoing decomposition. It combines with chlorine to form the tetrachloride, which is a thick honey-yellow liquid. When the dichloride is boiled with soda solution, *arsenorthotolyl oxide*, $CH_3C_6H_4AsO$, is formed as a powder which separated from the para-compound by re-crystallization from benzene.[1] In order to prepare it, bromotoluene to which a little acetic ether and petroleum have been added, is boiled with 1·5 per cent. sodium amalgam for a long time in an apparatus connected with an inverted condenser, and the products separated by re-crystallization from hot benzene.[2]

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[1] La Coste, *ibid.* ccviii. 18.

Mercury orthotolyl, $(CH_3C_6H_4)_2Hg$, is more readily soluble in benzene than the para-compound and crystallizes in large triclinic tablets melting at 107°.

Mercury paratolyl forms matted needles which melt at 238° and can be distilled without decomposition, if the heating be very carefully performed. It is only slightly soluble in cold water. Its derivatives resemble those of mercury phenyl.

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[1] *Ann. Chem. Pharm.* clxxiii. 162.

[2] *Ibid.* cci. 246

BENZYL GROUP.

2064 The compounds obtained by the replacement of one atom of hydrogen in the methyl group of toluene by other elements or radicals are looked upon as derivatives of a monovalent radical *phenylmethyl* or *benzyl*, $C_6H_5.CH_2$.

BENZYL ALCOHOL, $C_6H_5.CH_2.OH$.

Liebig and Wöhler, in 1832, observed that when oil of bitter almonds, C_7H_6O, is treated with alcoholic potash in absence of air, benzoic acid, $C_7H_6O_2$, is formed, together with an oily substance, which is different from the original oil; they make the following remarks: "Although we have not investigated this new product more carefully, there can be no doubt, provided that the alcohol takes no essential part in the reaction, that it is formed either by separation of oxygen from the oil of bitter almonds or by some reaction involving the sharing of the elements of water. In the former case its composition will be expressed by the formula $C_{14}H_{12}O$, in the latter by $C_{14}H_{14}O_2$"[1] ($C = 6$, $O = 8$).

Cannizzaro then found that this substance is "the alcohol corresponding to benzoic acid," and that although its composition does not correspond with that of the ordinary alcohols, it behaves towards reagents as an alcohol, the aldehyde of which would be oil of bitter almonds. He obtained the latter compound by oxidizing the alcohol with ordinary nitric acid, while chromic acid gave benzoic acid. He further showed that the action of hydrochloric acid produced an ethereal chlorine compound, C_7H_7Cl, which is derived from the alcohol of benzoic acid and is reconverted into the alcohol by treatment with caustic potash; when heated with alcoholic ammonia it yielded a base which differed essentially from toluidine. He also prepared the acetate, which is decomposed by warming with caustic potash into acetic acid and the alcohol of benzoic acid, and says: "This kind of alcohol appears to be the type of a whole class of new alcohols, the more complete investigation of which is now in progress."[1]

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[1] *Ann. Chem. Pharm.* iii. 254, 261.

In the course of this investigation he found that concentrated alcoholic potash produced a decomposition in which benzoic acid and toluene were formed from the alcohol, so that the latter stands in the same relation to toluene as wood-spirit to marsh gas:[2]

$$C_7H_8O + KOH = C_7H_5KO_2 + 2H_2$$
$$C_7H_8O + H_2 = C_7H_8 + H_2O.$$

He also succeeded in converting toluene into the alcohol; by the action of chlorine on the boiling hydrocarbon he obtained chlorobenzyl, which was identical with that obtained by the action of hydrochloric acid on the alcohol. On heating with potassium acetate, both compounds gave benzyl acetate, which yielded the alcohol on saponification with caustic potash.[3]

This compound had previously been in the hands of several chemists, who had not, however, recognised its nature. Fremy isolated from Peru balsam a compound which he named cinnameïn, from which he obtained cinnamic acid and peruvin, $C_9H_{12}O$, by heating with caustic potash.[4] The latter compound, according to Plantamour, who prepared it the same way and also observed the formation of cinnamic acid, is ethyl cinnamate; he was led to this conclusion by the fact that when he heated it with caustic potash and evaporated the whole to dryness, he obtained potassium cinnamate and a combustible vapour which he took for ethyl alcohol. He remarks that the origin of this substance, which was only recognised in this indirect and remarkable manner, still requires explanation.[5] Scharling first accurately determined the composition of cinnameïn and looked upon it as a compound ether. The peruvin, C_7H_8O, obtained from it he considered as an alcohol, probably identical with Cannizzaro's compound. When he brought it into contact with platinum black, the smell of oil of bitter almonds was produced.[6]

Strecker then expressed his conviction that cinnameïn is the cinnamic ether of benzyl alcohol,[7] and was confirmed by Kraut, according to whom Fremy's peruvin was a mixture of this alcohol and toluene, Plantamour's compound being, however, the pure alcohol. The acid taken for cinnamic acid was obviously benzoic acid and the combustible vapour consisted of toluene.[1]

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[1] *Ann. Chem. Pharm.* lxxxviii. 129.

[2] *Ibid.* xc. 252.

[3] *Ibid* xcvi. 246.

[4] *Ibid.* xxx. 324.

[5] *Ibid.* xxx. 341.

[6] *Ibid.* xcvii. 168.

[7] *Lehrb. Org. Chem.* 1856, 456.

The liquid portion of Peru balsam[2] consists chiefly of the benzoate and cinnamate of benzyl, but also contains some free benzyl alcohol.[3] Both ethereal salts occur in Tolu balsam,[4] and the latter in liquid styrax.[5]

Benzyl alcohol also seems to be contained in the oil of the cherry-laurel, which consists chiefly of benzaldehyde and its cyanhydrin (Tilden).[6]

The action of alcoholic potash on oil of bitter almonds, which was observed by Cannizzaro, is characteristic of the aromatic aldehydes, oxidation and reduction taking place simultaneously:

$$C_6H_5.CHO + KOH = C_6H_5.CO.OK + H_2$$
$$C_6H_5.CHO + H_2 = C_6H_5.CH_2.OH.$$

Benzyl alcohol is also formed by the action of sodium amalgam and water on benzaldehyde[7] and on benzoic acid,[8] while the fatty acids are not changed by nascent hydrogen. Benzoyl chloride, $C_6H_5.COCl$, is also reduced to benzyl alcohol by the action of sodium amalgam and hydrochloric acid,[9] while a better yield may be obtained by adding sodium amalgam to an ethereal solution of benzamide, $C_6H_5.CONH_2$, which contains water and has been rendered faintly acid with hydrochloric acid.[10]

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[1] *Ann. Chem. Pharm.* cvii. 208.

[2] Peru balsam, like Tolu balsam, was first described by the Spanish physician Monardes (p. 3); the latter is derived from *Myroxylon toluifera*, the former from *Myroxylon pareirae*, a native of Central America in the district of Costa del Balsamo. Peru balsam contains the same substances as that from Tolu, together with several of a different nature, this being due to the difference in the methods of extraction employed in the two cases. While the latter is obtained by the simple process of making incisions, it is necessary to remove the bark before extracting the Peru balsam. In order to accomplish this, it is first loosened by blows of a hammer or the back of an axe, and is then superficially charred by burning torches or bundles of twigs, the effect of this treatment being either to detach it or to render its removal a matter of no difficulty. The stem is next wrapped round with rags, which become saturated with the balsam, and are then removed and heated with water; the balsam is thus separated from the cloth and sinks to the bottom of the vessel (Flückiger and Hanbury, *Pharmacographia*, 2 Ed. p. 205).

[3] Kraut, *Ann. Chem. Pharm.* clii. 131.

[4] *Ber. Deutsch. Chem. Ges.* ix. 830.

[5] Laubenheimer, *Ann. Chem. Pharm.* clxiv. 289.

[6] *Pharm. Journ. Trans.* [3] v. 761.

[7] Friedel, *Ann. Chem. Pharm.* cxxiv. 324.

[8] Herrmann, *ibid.* cxxxii. 75.

[9] Lippmann, *ibid.* cxxxvii. 252.

[10] Guareschi, *Gazz. Chim. Ital.* iv. 465; *Ber. Deutsch. Chem. Ges,* vii. 1462.

It is best obtained from benzyl chloride, which can readily be prepared from toluene, by boiling it for two hours with water and lead hydroxide,[1] or by simply boiling it for two days with 25—30 parts of water, 76 per cent. of the theoretical yield being thus obtained.[2]

According to Mennier, it may be advantageously prepared by boiling equal parts of benzyl chloride and potassium carbonate with 10 parts of water for several hours.[3]

Cannizzaro's process does not serve for the preparation of the alcohol from benzaldehyde, as the action of the alcoholic potash is only gradual, even on long continued heating, and a considerable loss is experienced through the formation of resinous products. If, however, 10 parts of the aldehyde be shaken up with a solution of 9 parts of caustic potash in 6 parts of water until a permanent emulsion is obtained, and sufficient water to form a clear solution be then added to the semi-solid mass of crystals formed on standing by the separation of potassium benzoate, the benzyl alcohol can readily be extracted from the liquid with ether. The ether is then distilled off and the residue purified by rectification without being dried. In this way 92 per cent. of the theoretical yield can be obtained, while the application of alcoholic potash only gives a yield of 43 per cent. Since only one half of the benzaldehyde is converted into the alcohol, benzyl chloride is a more economical source; it is, however, more difficult to obtain in a state of purity than benzaldehyde and therefore does not yield a pure product so readily. As mentioned above, it is impossible to dry the alcohol before distillation; it combines with calcium chloride slowly in the cold, more rapidly on heating, and is attacked by solid caustic potash.[4]

If two molecules of benzaldehyde be added to a solution of one atom of sodium in 12 parts of methyl alcohol and the mixture heated in an apparatus connected with inverted condenser, a white substance soon separates out, which seems to be a compound of methyl benzoate and sodium methylate, since it is formed when these are heated together. If the heating be continued for about two days and the mass neutralized with glacial acetic acid, and then heated with water, an oil separates out which can be separated into two portions by distillation. About two-thirds of the whole boil between 198°—210°, and consist of a mixture of equal molecules of methyl benzoate, boiling at 199°, and benzyl alcohol, boiling at 206°. These cannot be separated, but if the benzoate be saponified, pure benzyl alcohol can readily be obtained.

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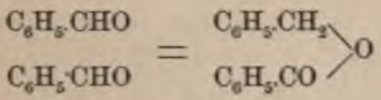
[1] Grimaux and Lauth, *Ann. Chem. Pharm.* cxliii. 80.
[2] Niederist, *ibid.* cxcvi. 353.
[3] *Bull. Soc. Chim.* xxxviii. 159.
[4] R. Meyer, *Ber. Deutsch. Chem. Ges.* xix. 2394.

The smaller portion of the product, about 20—30 per cent. on the benzaldehyde employed, boils at 320°—324°, and consists of benzyl benzoate. This is polymeric with the aldehyde and is formed directly from it:



$$\begin{array}{l} C_6H_5.CHO \\ C_6H_5.CHO \end{array} = \left.\begin{array}{l} C_6H_5.CH_2 \\ C_6H_5.CO \end{array}\right\rangle O$$

The chief reaction, however, consists in the conversion of the benzaldehyde in the presence of sodium methylate into methyl benzoate and benzyl alcohol:

$$2C_6H_5.CHO + CH_3.OH = C_6H_5.CO.OCH_3 + C_6H_5.CH_2.OH.$$

The two latter appear to be then partially converted into benzyl benzoate and methyl alcohol.[1]

If this reaction be employed for the preparation of benzyl alcohol, the original product is simply saponified.

In order to prepare it from Peru balsam, the latter is thoroughly agitated with 2 volumes of caustic potash of sp. gr. 1·2, the emulsion exhausted with ether, the extract separated and evaporated, and the residual oil heated with 4 volumes of caustic potash of sp. gr. 1·3 until a homogeneous liquid is obtained. The pulpy mass of crystals formed on cooling is pressed in linen, and the liquid diluted with water and distilled until the distillate ceases to appear milky. The alcohol is then separated from the aqueous distillate and the portion which remains dissolved in the latter extracted by ether.[2]

Properties.—Benzyl alcohol is a liquid which possesses a faint aromatic odour, boils at 206°, and has a sp. gr. of 1·063 at 0°. It is not insoluble in water, as was at one time thought, for 100 parts of water at 17° dissolve 4 parts (R. Meyer). When heated with hydriodic acid and a little phosphorus to 170°—180°, it is almost completely reduced to toluene, only a small amount of higher boiling substances being formed.[1] Its other characteristic properties which were ascertained by Cannizzaro have been already mentioned.

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[1] L. Claisen, private communication.

[2] Kachler, *Ber. Deutsch. Chem. Ges.* ii. 512.

BENZYL ETHERS.

2065 *Benzyl methyl ether*, $C_6H_5.CH_2.O.CH_3$, was obtained by Sintenis by heating benzyl chloride with methyl alcohol and caustic potash.[2] It is a pleasant smelling liquid, which boils at 167°—168° and is decomposed by chlorine in the cold with formation of benzaldehyde and methyl chloride :

$$C_6H_5.CH_2.O.CH_3 + Cl_2 = C_6H_5.COH + CH_3Cl + HCl.$$

Benzyl ethyl ether, $C_6H_5.CH_2.O.C_2H_5$, is formed when benzyl chloride is boiled with alcoholic potash, and is a mobile liquid, possessing a pleasant odour and boiling at 182°—184°.[3] Chlorine acts upon it in the cold just as on the methyl ether; at the boiling point, however, benzoyl chloride is formed:

$$C_6H_5.CH_2.O.C_2H_5 + 2Cl_2 = C_6H_5.COCl + C_2H_5Cl + 2HCl.$$

In the presence of iodine, ethyl iodide and parachlorobenzaldehyde, $C_6H_4Cl.COH$, are obtained (Sintenis).

Bromine produces a similar decomposition, benzaldehyde, ethyl bromide and hydrobromic acid being first formed; the latter then decomposes another portion of the ether into benzyl bromide and ethyl bromide, and the benzaldehyde is converted into benzoyl bromide by the excess of bromine.[4]

Dibenzyl ether or *Benzyl oxide*, $(C_6H_5.CH_2)_2O$. Cannizzaro obtained this compound by heating benzyl alcohol to 120°—125° with boron trioxide and treating the product with water and potassium carbonate. When the dried oil is distilled, unaltered benzyl alcohol comes over first, and then the ether, a resinous hydrocarbon remaining behind in the retort. Dibenzyl ether is a colourless, oily liquid, which boils at 310°—315° and has a faint indigo-blue fluorescence. It decomposes into toluene and benzaldehyde when heated to a few degrees above 315° in a sealed tube; a very small quantity of the resinous hydrocarbon is also formed in this way. Dibenzyl ether is also formed in small quantity, together with various hydrocarbons, when benzyl chloride is heated with water to 190°.[1]

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[1] Gräbe, *Ber. Deutsch. Chem. Ges.* viii. 1054.

[2] *Ann. Chem. Pharm.* clxi. 334.

[3] Cannizzaro, *Jahresb.* 1856, 582.

[4] Paterno, *Gaz. Chim. Ital.* i. 586.

C. W. Lowe prepared dibenzyl ether in the following way:—Sodium was added to benzyl alcohol diluted with ether. Towards the end of the reaction heat was applied in order to convert all the alcohol into sodium benzylate. The product was mixed with benzyl chloride and gently heated, when a rather violent reaction set in.

Dibenzyl ether is a perfectly colourless liquid, having a slight but persistent odour of hawthorn blossom. Its sp. gr. at 16° is 1·0359. It boils at 295°—298°, at the same time being partially resolved into toluene and benzaldehyde. This decomposition goes on more rapidly at 315° as Cannizzaro found, a very small quantity of a resinous body being formed at the same time.

Benzyl phenyl ether, $C_6H_5.CH_2.O.C_6H_5$, is obtained by heating benzyl chloride with potassium phenate and alcohol to 100°.[2] It forms scaly crystals with a nacreous lustre, melts at 38°—39° and boils at 286°—287° (Sintenis). On heating with concentrated hydrochloric acid to 100°, it decomposes into benzyl chloride and phenol; hydrobromic acid produces a similar decomposition. Chlorine attacks it in the cold with formation of benzyl chloride and substitution products of phenol, the action of bromine being quite analogous. In the presence of mercuric oxide, on the other hand, substitution products of the ether are formed (Sintenis).

			Melting-point.	Boiling-point.
Benzyl chloro-phenyl ether	$\left.\begin{matrix}C_6H_5.CH_2\\C_6H_4Cl\end{matrix}\right\}O$	long needles	70°—71°	—
Benzyl bromo-phenyl ether	$\left.\begin{matrix}C_6H_5.CH_2\\C_6H_4Br\end{matrix}\right\}O$	long needles	59°—59·5°	—
Benzyl ortho-cresyl ether[3]	$\left.\begin{matrix}C_6H_5.CH_2\\CH_3.C_6H_4\end{matrix}\right\}O$	liquid	—	285°—290°
Benzyl para-cresyl ether	$\left.\begin{matrix}C_6H_5.CH_2\\CH_3.C_6H_4\end{matrix}\right\}O$	hexagonal prisms	41°	—

Ethers of benzyl with the dihydroxybenzenes are formed when the latter are heated with benzyl bromide and alcoholic potash.[1]

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[1] Limpricht, *Ann. Chem. Pharm.* cxxxix. 307.
[2] Lauth and Grimaux, *ibid.* cxliii. 81.
[3] Städel, *Ber. Deutsch. Chem. Ges.* xiv. 898.

			Melting-point.
Benzylquinol,	$C_6H_4\left\{\begin{matrix}OH\\O.CH_2.C_6H_5\end{matrix}\right\}$	large lustrous scales	122°
Dibenzylquinol,	$C_6H_4(O.CH_2.C_6H_5)_2$,	lustrous tablets	130°
Dibenzylresorcinol,	$C_6H_4(O.CH_2.C_6H_5)_2$,	small lustrous tablets	76°
Dibenzylcatechol,	$C_6H_4(O.CH_2.C_6H_5)_2$,	yellow needles	61°

ETHEREAL SALTS OF BENZYL.

2066 *Benzyl chloride*, $C_6H_5.CH_2Cl$. Cannizzaro obtained this compound by the action of hydrochloric acid on benzyl alcohol and it is also formed by that of chlorine on boiling toluene.[2]

It is prepared on the large scale by the latter method, the toluene being contained in large glass balloons heated by a bath of calcium chloride, and the chlorine passed through in such a manner that it chiefly comes in contact with the vapour of the toluene. This is effected by only allowing the leaden conducting tube, which terminates in a short piece of glass tubing, to dip a small distance below the surface of the boiling liquid. The vapours of toluene are condensed by a cooling arrangement and the hydrochloric acid evolved is led into water. The product is washed with water containing a little caustic soda, and the benzyl chloride freed from unaltered toluene and higher substitution products by distillation.

It is a colourless liquid, the vapour of which has a penetrating aromatic smell, rapidly produces a flow of tears and attacks the mucous membrane most violently. It boils at 176° and has a sp. gr. of 1·107 at 14°. As it undergoes double decomposition very readily, it is employed for the preparation of the other benzyl compounds, and it is also used to a considerable extent in the synthesis of the higher members of the aromatic series. It is also technically employed in the manufacture of benzaldehyde and in the colour industry.

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[1] Schiff and Pellizzari, *Ann. Chem. Pharm.* ccxxi. 365.

[2] Beilstein and Geitner, *ibid.* cxxxix. 337.

Benzyl bromide, $C_6H_5.CH_2Br$, is formed by the action of hydrobromic acid on benzyl alcohol, and by that of bromine on boiling toluene.[1] It is a liquid which first smells like cress and then like mustard oil; its vapour, like that of the chloride, produces a flow of tears. It boils at 198°—199°, and has a sp. gr. of 1·438 at 22°.

Benzyl iodide, $C_6H_5.CH_2I$, was obtained by Cannizzaro in the impure state by the action of iodine and phosphorus on benzyl alcohol. Lieben prepared the pure compound by allowing benzyl chloride to stand in the dark for three weeks with five times its weight of hydriodic acid.[2] It is also formed by the action of potassium iodide on benzyl chloride,[3] and is a colourless, crystalline body, the vapour of which produces a most copious flow of tears; it is only slightly soluble in alcohol, but readily in ether and carbon disulphide. It fuses at 24° to a liquid which has a sp. gr. of 1·7335, and on further heating becomes coloured red, decomposing at about 240°, at which temperature it commences to boil, into iodine, hydriodic acid, and a hydrocarbon which smells like toluene.

Benzyl nitrate, $C_6H_5.CH_2.NO_3$. appears to be formed by the action of silver nitrate on benzyl chloride: the product of the reaction decomposes on distillation with an energetic evolution of red fumes, the distillate consisting of benzaldehyde and benzoic acid.[4]

The same products are obtained by treating benzyl iodide with silver nitrite.[5]

2067 *Benzyl acetate*, $C_6H_5.CH_2\,C_2H_3O_2$. Cannizzaro obtained this compound by distilling benzyl alcohol with acetic and sulphuric acids, as well as by heating benzyl chloride with potassium acetate, and alcohol. It is a liquid which possesses an aromatic odour, boils at 206°, and has a sp. gr. of 1·057 at 16·5°.[6] It is converted into the benzyl ether of hydrocinnamic acid or benzylacetic acid by the action of sodium:

$$4C_6H_5.CH_2.O.CO.CH_3+2Na =$$
$$2C_6H_5.CH_2.O.CO.CH_2.CH_2.C_6H_5+2NaO.CO.CH_3+H_2.$$

		Boiling-point.
Benzyl propionate,	$C_7H_7.O.C_3H_5O$	219°—220°.
Benzyl butyrate,	$C_7H_7.OC_4H_7O$	238°—240°.

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[1] Kekulé, *Ann. Chem. Pharm.* cxxxvii. 139; Cannizzaro, *ibid.* cxli. 198; Beilstein, *ibid.* cxliii. 369; Lauth and Grimaux, *ibid.* cxlv. 113.

[2] *Zeitschr. Chem.* [2] vi. 736.

[3] V. Meyer, *Ber. Deutsch. Chem. Ges.* x. 311.

[4] Brunner, *Ber. Deutsch. Chem. Ges.* ix. 1744.

[5] van Renesse, *ibid.* ix. 1454.

[6] Conrad and Hodgkinson, *Liebig's Ann.* cxciii. 298.

These ethers are acted upon by sodium in the same way as the acetate (Conrad and Hodgkinson). The compounds thus formed will be subsequently described.

Benzyl oxalate, $(C_6H_5.CH_2)_2C_2O_4$, is formed by the action of benzyl chloride on silver oxalate,[1] and by heating benzyl alcohol with oxalic acid.[2] It crystallizes from hot alcohol in lustrous white, scaly crystals, melting at 80·5°.

Isonitrosobenzyl ether, $C_6H_5.CH_2.O.N{=}CH.CO.CH_3$, is prepared by heating benzyl chloride with a solution of sodium and isonitroso-acetone (Part I. p. 572, and Part III. p. 170, *note*) in absolute alcohol. It crystallizes from petroleum ether in colourless tablets, which have a pleasant smell of flowers and melt at 45°—46°.[3]

Acetoxime benzyl ether, $C_6H_5.CH_2.ON{=}C(CH_3)_2$, is obtained in a similar manner from acetoxime, and is a pleasant smelling liquid which decomposes into acetone and benzylhydroxylamine when boiled with concentrated hydrochloric acid:

$$C_6H_5.CH_2.O.N{=}C(CH_3)_2+H_2O=C_6H_5.CH_2.O.NH + CO(CH_3)_2$$

The compound actually obtained in this way is *benzylhydroxy-ammonium chloride*, which crystallizes in silvery scales, and is converted into benzyl iodide by heating with hydriodic acid:[4]

$$C_6H_5.CH_2.O.NH_3Cl+3HI=C_6H_5.CH_2I+NH_4Cl+H_2O+I_2$$

SUBSTITUTION PRODUCTS OF BENZYL ALCOHOL AND ITS DERIVATIVES.

2068 Substitution-products are not formed by the direc action of chlorine, bromine, or nitric acid on benzyl alcohol since all these reagents produce oxidation. Its ethers, how ever, can undergo direct substitution, and if an atom hydrogen in one of them be replaced, para-compounds ar formed, from which the corresponding alcohols may readil be obtained. Thus, parachlorobenzyl alcohol, $C_6H_4Cl.CH_2.OH$, is prepared by boiling its chloride or bromide with water:

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[1] Beilstein and Kuhlberg, *Liebig's Ann.* cxlvii. 341.
[2] Dumas and Demarçay, *Compt. Rend.* lxxxiii. 688.
[3] Meyer and Ceresole, *Ber. Deutsch. Chem. Ges.* xv. 3071.
[4] Janny, *ibid.* xvi. 170.

$$C_6H_4Cl.CH_2Br + H_2O = C_6H_4Cl.CH_2OH + HBr.$$

The haloid ethers can also be converted into the acetate by boiling with alcohol and potassium acetate, and this saponified by heating with ammonia:

$$C_6H_4Cl.CH_2.O.C_2H_3O + NH_3 = C_6H_4Cl.CH_2.OH + C_2H_3O.NH_2.$$

The higher chlorinated benzyl chlorides have been converted into their alcohols by means of this reaction.

Paranitrobenzyl alcohol can readily be prepared by nitrating benzyl acetate or oxalate and heating the product with ammonia.

Chlorine substitution-products of benzyl chloride can be obtained, as already mentioned, by treating it with chlorine in the cold or in presence of iodine, as well as by allowing chlorine to act upon the vapour of boiling, chlorinated toluene. According to Beilstein and Kuhlberg, the latter is the better method, and is now generally adopted.

The bromine substitution-products are prepared in a similar manner; the use of this method has shown that substitution does not readily take place in the methyl group when bromine is allowed to act on boiling orthobromotoluene.

Paranitrotoluene is converted by bromine at high temperatures into paranitrobenzyl bromide; paranitrobenzyl chloride and metanitrobenzyl bromide can also be readily obtained, but not the ortho-compound. If orthonitrotoluene be heated with bromine, no orthonitrobenzyl bromide is found, but the product, according to Wachendorff, consists of dibromorthonitrotoluene, $C_6H_2Br_2(NO_2)CH_3$, which is not attacked by potassium acetate or silver acetate even at 160°.[1] It possesses the exceptional property of dissolving in aqueous alkalis and being reprecipitated by mineral acids, and Greiff was therefore induced to examine it more carefully. He found that it is not dibromonitrotoluene, but the isomeric dibromortho-amidobenzoic acid, $C_6H_2Br_2(NH_2)CO_2H$. Since the isomerides of orthonitrotoluene behave quite differently towards bromine, it follows that the ortho-position facilitates a mutual exchange between the oxygen of the nitroxyl and the hydrogen of the methyl. How this intermolecular change takes place has not yet been explained, but it seems probable that ortho-nitrobenzyl bromide is first formed and is then converted by the nitro-group into ortho-amidobenzoic acid, just as benzyl chloride is oxidized to benzoic acid by nitric acid.

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[1] *Ann. Chem. Pharm.* clxxxv. 259.

Parachlorobenzyl alcohol, $C_6H_4Cl.CH_2OH$, is formed by boiling the corresponding bromide or chloride with water,[1] or by heating parachlorobenzyl acetate to 1[illegible]° with aqueous ammonia.[2] It is readily soluble in alcohol, scarcely in cold, but somewhat more readily in warm water, from which it crystallizes in long needles melting at [illegible] (Jackson and Field). Oxidizing agents convert it into parachlorobenzoic acid.

			Melting-point.
Dichlorobenzyl alcohol,[3]	$C_6H_3Cl_2.CH_2OH$.	needles	77°
Trichlorobenzyl alcohol,[4]	$C_6H_2Cl_3.CH_2OH$.	crystals	—
Tetrachlorobenzyl alcohol,[5]	$C_6HCl_4.CH_2OH$.	..	—
Pentachlorobenzyl alcohol,[6]	$C_6Cl_5.CH_2OH$.	short needles	193°

Parachlorobenzyl ethyl ether, $C_6H_4Cl.CH_2.O.C_2H_5$, is formed by heating parachlorobenzyl chloride[7] or parachlorobenzyl acetate[8] with alcoholic potash. It is a liquid which boils at 218°,[9] and is split up by chlorine in the cold into ethyl chloride and parachlorobenzaldehyde.

Phenylchloromethyl ethyl ether, or Ethoxybenzyl chloride, $C_6H_5.CHCl.OC_2H_5$, is prepared by boiling benzylidene chloride, $C_6H_5.CHCl_2$, for a long time with alcoholic ammonia. It is a liquid which boils at 21[illegible]°—212° and is converted into ethyl metanitrobenzoate, $C_6H_4.NO_2.CO.OC_2H_5$, by nitric acid.[10]

Parachlorobenzyl chloride, $C_6H_4Cl.CH_2Cl$, is obtained together with a little of the ortho-compound, by the chlorination of benzyl chloride in presence of iodine, and by the action of chlorine on boiling monochlorotoluene, as a liquid which boils at 213°—214°.[11] It is prepared pure from parachlorotoluene;[12] it crystallizes from alcohol in lustrous needles or prisms which melt at 29°, readily sublime, and possess an aromatic vapour which attacks the mucous membrane very violently.

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[1] Jackson and Field, *Ber. Deutsch. Chem. Ges.* xi. 905; *Amer. Chem. Journ* ii. 88.

[2] Beilstein and Kuhlberg, *Ann. Chem. Pharm.* cxlvii. 344.

[3] *Ibid.* 350.

[4] *Ibid.* clii. 241.

[5] *Ibid.* 245.

[6] *Ibid.* 246

[7] Naquet, *ibid.* Suppl. [2] 250.

[8] Neuhof, *ibid.* cxlvii. 345

[9] Sintenis, *ibid.* clxi. 335.

[10] Hubner and Bente, *Ber. Deutsch. Chem. Ges.* vi. 805.

[11] Neuhof, *Ann. Chem. Pharm.* cxlvi. 320.

[12] Jackson and Field, *Ber. Deutsch. Chem. Ges.* xi. 904.

			Melting-point.	Boiling-point.
Dichlorobenzyl-chloride,[1]	$C_6H_3Cl_2.CH_2Cl$	liquid . .	—	241°[1]
Trichlorobenzyl-chloride,[2]	$C_6H_2Cl_3.CH_2Cl$	. . .	—	273°
Tetrachlorobenzyl-chloride,[3]	$C_6HCl_4.CH_2Cl$	. . .	—	296°
Pentachlorobenzyl-chloride,[4]	$C_6Cl_5.CH_2Cl$,	fine needles	103°	325°—327°

Parachlorobenzyl bromide, $C_6H_4Cl.CH_2Br$, resembles the chloride very closely; it melts at 48·5°.[5]

Parachlorobenzyl acetate, $C_6H_4Cl.CH_2.O.C_2H_3O$, is obtained by boiling the chloride with potassium acetate and absolute alcohol; it is a liquid which boils at 240° and has an aromatic odour.[6]

Parabromobenzyl alcohol, $C_6H_4Br.CH_2.OH$, is formed when the bromide is boiled with water for several days; it crystallizes from a hot solution in flat, elastic, pearly needles which have an aromatic odour, melt at 69°, and only volatilize slowly with steam.[7]

Parabromobenzyl bromide, $C_6H_4Br.CH_2Br$. This compound is prepared by passing bromine vapour into a boiling mixture of parabromotoluene and orthobromotoluene, which is obtained by the direct bromination of toluene. After the calculated quantity has been added, the liquid is allowed to cool, a portion of the bromide crystallizing out in large, rhombic prisms. The mother-liquor is then distilled with steam in which the ortho- is more readily volatile than the para-compound. The latter can also readily be obtained in long, thick, transparent prisms by allowing bromine to act upon the mixture of bromotoluenes in the sunlight.[8] Parabromobenzyl bromide crystallizes from alcohol in needles which melt at 61° and are volatile with steam; its vapour has a pleasant, aromatic odour, but attacks the eyes, nose, and throat very violently.[1]

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[1] Beilstein and Kuhlberg, *Ann. Chem. Pharm.* cxlvi. 146, 320.

[2] *Ibid.* cl. 290. [3] *Ibid.* 299. [4] *Ibid.* 302.

[5] Field and Jackson, *loc. cit.*

[6] Neuhof, *Ann. Chem. Pharm.* cxlvii. 345.

[7] Jackson and Lowry, *Ber. Deutsch. Chem. Ges.* x. 1209.

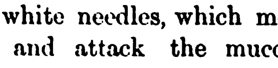
[8] Schramm, *ibid.* xvii. 2922; xviii. 350.

Parabromobenzyl acetate, $C_6H_4Br.CH_2.O.C_2H_3O$, is a liquid which has a pleasant smell resembling that of acetic ether, and decomposes on distillation.[2]

Metabromobenzyl bromide, $C_6H_4Br.CH_2Br$, is obtained in a similar manner to the para-compound; the yield is, however, very poor. It crystallizes in plates or needles which melt at 41°, and its vapour attacks the mucous membrane violently, but has a somewhat different smell from that of the para-compound. It only volatilizes slowly in a current of steam, but with remarkable rapidity in ether and tolerably readily in alcohol. It is not attacked by chromic acid solution, but the corresponding alcohol, which has not been further investigated, is oxidized by it to metabromobenzoic acid.[3]

Orthobromobenzyl alcohol, $C_6H_4Br.CH_2.OH$, crystallizes from hot water in flat needles, which melt at 80°, and readily volatilize with steam.[4]

Orthobromobenzyl bromide, $C_6H_4Br.CH_2Br$, is only formed with difficulty, and has not been obtained pure, since it decomposes on distillation. It is an oily liquid, which does not solidify at −15°, volatilizes with steam, possesses an aromatic odour, and rapidly attacks the mucous membrane; a drop placed on the tongue causes severe pain.[5] Sodium acts upon its ethereal solution with formation of various products, among them being anthracene:



$$C_6H_4 \begin{array}{c} \diagup CH \diagdown \\ | \\ \diagdown CH \diagup \end{array} C_6H_4.$$

Para-iodobenzyl alcohol, $C_6H_4I.CH_2.OH$, crystallizes from carbon disulphide in scales and from boiling water in long needles, which have an aromatic odour and melt at 71·7°.[6]

Para-iodobenzyl bromide, $C_6H_4I.CH_2Br$, is formed by the action of bromine vapour on heated para-iodotoluene, and crystallizes from alcohol in flat, white needles, which melt at 78·7°, possess an aromatic odour, and attack the mucous membrane less violently than the bromobenzyl bromides. Boiling water converts it into the alcohol.[7]

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[1] Schramm, *Ber. Deutsch. Chem. Ges.* viii. 1672; ix. 931.

[2] Jackson and Lowry, *ibid.* x. 1209.

[3] Jackson and White, *Amer. Chem. Journ.* ii. 315. [4] Jackson, *ibid.* viii. 932.

[5] Jackson, *Ber. Deutsch. Chem. Ges.* ix. 932.

[6] Jackson and Mabery, *ibid.* xi. 56; *Amer. Chem. Journ.* ii. 251.

[7] Jackson and Mabery, *loc. cit.*

2070 *Paranitrobenzyl alcohol*, $C_6H_4(NO_2)CH_2.OH$, is prepared by heating its acetate or oxalate with ammonia to 100°,[1] and by the action of caustic soda on paranitrobenzaldehyde.[2] It crystallizes from boiling water in fine, lustrous, colourless needles, which become coloured in the air and melt at 93°. On oxidation it yields paranitrobenzoic acid.

Paranitrobenzyl chloride, $C_6H_4(NO_2).CH_2Cl$, is obtained, together with the ortho- and meta-compounds, by the action of concentrated nitric acid on benzyl chloride,[3] the chloride being gradually added to the acid which has been previously cooled to −15°.[4] It is also formed by treating paranitrotoluene with chlorine at 185°—190°.[5] It crystallizes from boiling alcohol in fine, white needles, or small, nacreous plates, which melt at 76°.

An alkaline solution of pyrogallol reduces it to paranitrotoluene.[6]

Paranitrobenzyl bromide, $C_6H_4(NO_2)CH_2Br$, is formed when paranitrotoluene is heated to 120°—130° with bromine; the reaction takes place at 70°—80° in the presence of ferrous bromide, which acts as a bromine carrier.[7] On the gradual evaporation of its solution in a mixture of ether and alcohol, it crystallizes in thin tablets, which melt at 99°—100°. It destroys the skin, producing a burning pain, and the vapour given off by its hot alcoholic solution attacks the mucous membrane most violently (Wachendorff).

Paranitrobenzyl iodide, $C_6H_4(NO_2)CH_2I$, is obtained by heating the chloride with potassium iodide and alcohol; it crystallizes in four-sided tablets, melting at 127°, and its vapour produces a flow of tears.[8]

Paranitrobenzyl nitrate, $C_6H_4(NO_2)CH_2NO_3$. Beilstein and Kuhlberg prepared this compound by the action of concentrated nitric acid on the alcohol, and believed that it was dinitrobenzyl alcohol. Städel found, however, that it loses nitric acid when heated with water to 100°, and that it yields paranitrobenzoic acid on oxidation,[9] and Orth prepared it by heating the chloride with alcohol and silver nitrate.[1] It crystallizes from hot water in fine, white needles, and from alcohol in long, flat needles, melting at 71°.

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[1] Beilstein and Kuhlberg, *Ann. Chem. Pharm.* cxlvii. 343.

[2] Basler, *Ber. Deutsch. Chem. Ges.* xvi. 2715.

[3] Beilstein and Geitner, *Ann. Chem. Pharm.* cxxxix. 327; Grimaux, *ibid.* cxlv. 146; Abelli, *Gaz. Chim. Ital.* xiii. 97.

[4] Strakosch, *Ber. Deutsch. Chem. Ges.* vi. 1056.

[5] Wachendorff, *Ann. Chem. Pharm.* clxxxv. 271.

[6] Pellizzari, *Ber. Deutsch. Chem. Ges.* xviii. Ref. 150.

[7] Scheufeln, *Ann. Chem. Pharm.* ccxxxi. 177.

[8] Kumpf, *ibid.* xvii. 1074.

[9] *Ibid.* xiv. 903.

Paranitrobenzyl acetate, $C_6H_4(NO_2)CH_2.C_2H_3O_2$, is obtained by dissolving benzyl acetate in well-cooled concentrated nitric acid (Beilstein and Kuhlberg) or by heating the chloride with potassium acetate and alcohol (Grimaux). It crystallizes from hot alcohol in long, pale yellow needles, melting at 78°.

Paranitrobenzyl oxalate, $(C_6H_4(NO_2)CH_2)_2C_2O_4$, was obtained by Beilstein and Kuhlberg by dissolving benzyl oxalate in concentrated nitric acid; on heating with aqueous ammonia it is converted into the alcohol.

2071 *Metanitrobenzyl alcohol*, $C_6H_4(NO_2)CH_2.OH$, was prepared by Grimaux, together with metanitrobenzoic acid, by the action of alcoholic potash on metanitrobenzaldehyde as a thick, oily liquid, which decomposes on heating, but boils at 178°—180° under a pressure of 3 mm.[2]

Metanitrobenzyl chloride, $C_6H_4(NO_2)CH_2Cl$, is formed by the action of phosphorus pentachloride on the alcohol; it crystallizes from hot petroleum ether in long, light yellow needles, which melt at 45°—47°, and produces painful irritation and burning on the skin.[3]

Orthonitrobenzyl alcohol, $C_6H_4(NO_2)CH_2.OH$. When orthonitrotoluene is given to a dog, it appears in the urine as orthonitrobenzoic acid, and as the urea salt of *uronitrotoluic acid*, $2C_{13}H_{15}NO_9.CO(NH_2)_2 + 5H_2O$, crystallizing in long needles, which are very readily soluble in water, slightly in cold alcohol, and insoluble in ether. On boiling this with baryta water and decomposing the barium salt formed with sulphuric acid, *uronitrotoluic acid*, $C_{13}H_{15}NO_9$, is obtained as a crystalline mass resembling asbestos, which is extremely soluble in water and alcohol and has a strongly acid reaction. On boiling with dilute sulphuric acid it decomposes into a syrupy acid and orthonitrobenzyl alcohol;[4] this compound can also be prepared by the action of caustic soda on orthonitrobenzaldehyde.[5] It is slightly soluble in water, readily in alcohol and ether, and crystallizes in long, fine needles, which melt at 74°, and can be sublimed, but detonate when rapidly heated.

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[1] Kumpf, xv. 1136.

[2] *Zeitschr. Chem.* 1867, 562.

[3] Gabriel and Borgmann, *Ber. Deutsch. Chem. Ges.* xvi. 2064.

[4] Jaffé, Hoppe-Seyler's *Zeitschr.* ii. 47.

[5] Friedländer and Henriques, *Ber. Deutsch. Chem. Ges.* xiv. 2801.

Orthonitrobenzyl chloride, $C_6H_4(NO_2)CH_2Cl$, is formed, as already mentioned, together with its isomerides, by the nitration of benzyl chloride, and was first isolated from the product by Kumpf.[1] It is also obtained by the action of phosphorus pentachloride on the alcohol.[2] It crystallizes from petroleum ether in large rhombohedra melting at 48°—49°.

Orthonitrobenzyl iodide, $C_6H_4(NO_2)CH_2I$, is prepared by heating the chloride with potassium iodide and alcohol; it forms rhombohedral plates melting at 75°, and its vapour causes a flow of tears.

Orthamidobenzyl alcohol, $C_6H_4(NH_2)CH_2.OH$, is obtained by the action of hydrochloric acid and zinc-dust on orthonitrobenzyl alcohol in alcoholic solution. It crystallizes from benzene in white needles, which melt at 82°, become coloured brown in the light or in the air, and have a faint smell resembling that of aniline.

It combines with acids forming soluble, crystallizable salts.[3]

SULPHUR COMPOUNDS OF BENZYL.

2072 *Benzyl hydrosulphide*, or *Benzyl mercaptan*, $C_6H_5.CH_2.SH$. Märcker obtained this compound by heating benzyl chloride or benzyl bromide with an alcoholic solution of potassium hydrosulphide.[4] Otto prepared it by the action of benzyl chloride on potassium thiosulphate,[5] and Böttinger by fusing thiobenzaldehyde, $C_6H_5.CSH$, with caustic potash, benzyl disulphide and a little benzoic acid being simultaneously formed.[6]

It is a colourless, powerfully refractive liquid which has an unpleasant smell of leeks, boils at 195°, and has a sp. gr. of 1·058 at 20°; its vapour produces a flow of tears. It gradually oxidizes in the air, more rapidly in the presence of ammonia to benzyl disulphide; an ethereal solution of bromine produces the same effect.

Mercury benzyl mercaptide, $(C_6H_5.CH_2S)_2Hg$, is formed by heating the hydrosulphide with mercuric oxide; it crystallizes from alcohol in long, silky needles. Mercuric chloride, in alcoholic solution, gives with the mercaptan a white precipitate of $C_6H_5.CH_2.S.HgCl$.

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[1] Friedländer and Henriques, xvii. 1073.

[2] Gabriel and Borgmann, *Ber. Deutsch. Chem. Ges.* xvi. 2064.

[3] Friedländer and Henriques, *ibid.* xv. 2109.

[4] *Ann. Chem. Pharm.* cxxxvi. 75.

[5] *Zeitschr. Chem.* [2] vi. 23.

[6] *Ber. Deutsch. Chem. Ges.* xii. 1055.

Lead benzyl mercaptide, $(C_6H_5.CH_2S)_2Pb$, is obtained in small yellow plates by mixing hot, alcoholic solutions of lead acetate and benzyl mercaptan.

Parachlorobenzyl hydrosulphide, $C_6H_4Cl.CH_2.SH$, is formed when parachlorobenzyl chloride is boiled with an alcoholic solution of potassium hydrosulphide. According to Beilstein, it is obtained in lustrous crystals, melting at 84°—85°,[1] while according to Jackson and White, it is an oily liquid which possesses a most repulsive and penetrating odour, and solidifies on cooling in crystals which melt at 19°—20°.[2]

Paranitrobenzyl hydrosulphide, $C_6H_4(NO_2)CH_2.SH$, crystallizes from alcohol in small, colourless, lustrous plates, melting at 140°.[3]

Benzyl ethyl sulphide, $C_6H_5.CH_2.S.C_2H_5$, is prepared by the action of ethyl iodide on a solution of sodium in benzyl hydrosulphide, and is a transparent liquid, which boils at 214°—216°,[4] and possesses a penetrating odour resembling that of ordinary mercaptan.

Orthobenzyl thioformate, $(C_6H_5.CH_2.S)_3CH$, is formed when an aqueous solution of sodium benzyl mercaptide is heated with chloroform; it separates from hot alcohol in colourless crystals, melting at 98°. When heated with fuming nitric acid to 250°, it is decomposed into benzyl mercaptan and formic acid.[5]

Benzyl sulphide, $(C_6H_5.CH_2)_2S$. Märcker obtained this compound by heating benzyl chloride with an alcoholic solution of potassium sulphide. It crystallizes from hot alcohol in large, dazzling white plates, and from ether or chloroform in large, thick, rhombic tablets,[6] melting at 49°.

On distillation it yields stilbene, $C_{14}H_{12}$, and sulphuretted hydrogen; dibenzyl, $C_{14}H_{14}$, tolallyl sulphide, $C_{14}H_{10}S$, and thionessal, $C_{28}H_{20}S$, are simultaneously formed.

Methyl iodide and benzyl sulphide react even in the cold, more rapidly on warming, with formation of *benzyldimethylsulphine iodide*, $C_6H_5.CH_2(CH_3)_2SI$, and trimethylsulphine iodide,

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[1] Beilstein, *Ann. Chem. Pharm.* cxvi. 347 ; cxlvii. 346.
[2] *Amer. Chem. Journ.* ii. 167.
[3] Strakosch, *Ber. Deutsch. Chem. Ges.* v. 598.
[4] Märcker, *Ann. Chem. Pharm.* cxl. 88.
[5] Dennstedt, *Ber. Deutsch. Chem. Ges.* xi. 2265.
[6] Forst, *Ann. Chem. Pharm.* clxxviii. 671.

$(CH_3)_3SI$. The first stage of the reaction is represented by the following equation:

$$2CH_3I + (C_6H_5.CH_2)_2S = (CH_3)_2S + 2C_6H_5.CH_2I.$$

The methyl sulphide then combines with the iodides forming the compounds mentioned. If the product be extracted with water, shaken up with silver chloride and the filtrate then fractionally precipitated with platinum chloride, *benzyl dimethylsulphine platinichloride*, $(C_6H_5.CH_2(CH_3)_2S)_2PtCl_6$, separates out first; it crystallizes from water in long, orange-red needles.[1]

Cahours,[2] who has also investigated the action of methyl iodide on benzyl sulphide, gives the following equation:

$$3CH_3I + (C_6H_5.CH_2)_2S = (CH_3)_3SI + 2C_6H_5.CH_2I.$$

Benzyl bromide and methyl sulphide, on the other hand, react in the following way:

$$C_6H_5.CH_2Br + 2(CH_3)_2S = (CH_3)_3SBr + C_6H_5.CH_2.S.CH_3.$$

If methyl alcohol be also present, benzyl methyl ether is formed instead of benzyl methyl sulphide:

$$C_6H_5.CH_2Br + (CH_3)_2S + 2CH_3.OH = \\ (CH_3)_3SBr + C_6H_5.CH_2.O.CH_3 + H_2O.$$

Benzyl oxysulphide, $(C_6H_5.CH_2)_2SO$, is formed by the action of concentrated nitric acid on the sulphide; it crystallizes from alcohol in small plates which have a satin lustre, melt at 133°,[3] and are converted into sulphuric acid and benzoic acid by the further action of nitric acid (Märcker).

Benzyl disulphide, $(C_6H_5.CH_2)_2S_2$, is best obtained by the action of bromine in ethereal solution on benzyl mercaptan, and is also formed when benzyl chloride is treated in alcoholic solution with potassium disulphide; it crystallizes from alcohol in small, lustrous plates, melting at 66°—67°. Nascent hydrogen reconverts it into benzyl mercaptan (Märcker). It is decomposed on heating, yielding the same products as benzyl sulphide.

Benzyl dioxysulphide, or *Dibenzyl sulphone*, $(C_6H_5.CH_2)_2SO_2$, is formed in small quantity in the preparation of potassium benzyl

[1] Schöller, *Ber. Deutsch. Chem. Ges.* vii. 1274.

[2] *Compt. Rend.* lxxx. 1319.

[3] Otto and Lüders, *Ber. Deutsch. Chem. Ges.* xiii. 1284.

sulphonate.[1] It may readily be obtained, however, by oxidizing benzyl oxysulphide with potassium permanganate and glacial acetic acid (Otto and Lüders); it is insoluble in water, and crystallizes from hot alcohol in flat needles, which melt at 150°.

2073 *Benzylsulphonic acid*, $C_6H_5.CH_2.SO_2.OH$. Böhler prepared this compound by boiling benzyl chloride for several hours with a concentrated solution of normal potassium sulphite, the potassium salt obtained being converted into the lead salt, and this decomposed with sulphuretted hydrogen.[2] It is a deliquescent crystalline mass, and is also formed by the oxidation of benzyl disulphide with nitric acid.[3] When it is fused with caustic potash, it yields benzoic acid (Vogt), together with some benzene and a larger quantity of toluene.[4]

Potassium benzylsulphonate, $C_6H_5.CH_2.SO_3K + H_2O$, crystallizes from hot water in well-developed rhombic prisms.

Barium benzylsulphonate, $(C_6H_5.CH_2.SO_3)_2Ba + 2H_2O$, is obtained by the addition of barium chloride to the solution of the potassium salt; it forms plates, which are only slightly soluble in water.

Lead benzylsulphonate, $(C_6H_5.CH_2.SO_3)_2Pb$. If the barium salt be decomposed with dilute sulphuric acid, and the hot filtrate saturated with lead hydroxide, the basic salt $C_6H_5.CH_2.SO_3.PbOH$, is obtained as a lustrous, crystalline precipitate, which is converted into the normal salt by carbon dioxide; this crystallizes from hot water in lustrous plates.

Potassium chlorobenzylsulphonate, $C_6H_4Cl.CH_2.SO_3K + H_2O$, is prepared from chlorobenzyl chloride and potassium sulphite, and crystallizes in needles; barium chloride added to the potassium salt yields *barium chlorobenzylsulphonate*, $(C_6H_4Cl.CH_2.SO_3)_2Ba + H_2O$, which forms colourless lustrous crystals.

When the potassium salt is fused with caustic potash, salicylic acid and parahydroxybenzoic acid are formed (Vogt and Henninger).

Benzylsulphonic chloride, $C_6H_5.CH_2.SO_2Cl$. Barbaglia endeavoured to prepare this compound by the distillation of potassium benzylsulphonate with phosphorus pentachloride, but only obtained benzyl chloride, together with phosphorus oxychloride and some thionyl chloride.[5] In order to prepare it, the potassium salt is treated with an equal weight of phosphorus chloride and the mixture gently warmed until the reaction is complete. The product is then washed with water and the residue crystallized from ether. Benzenesulphonic chloride forms colourless prisms, which melt at 92° and are decomposed when more strongly heated into benzyl chloride and sulphur dioxide; it is converted by ammonia into *benzylsulphonamide*, $C_6H_5.CH_2.SO_2.NH_2$, which crystallizes from water in prisms melting at 105°.[1]

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[1] Vogt and Henninger, *Ann. Chem. Pharm.* clxv. 375.

[2] *Ibid.* cliv. 50.

[3] Barbaglia, *Ber. Deutsch. Chem. Ges.* v. 687.

[4] Otto, *ibid.* xiii. 1288.

[5] *Ibid.* v. 270.

Nitrobenzylsulphonic acid, $C_6H_4(NO_2)CH_2.SO_3H$, is formed by the action of fuming nitric acid on barium benzylsulphate. A mixture is thus obtained which contains, together with the para-compound, a little of the orthonitro-acid and the dinitro-acid, which cannot be completely separated. On boiling with a mixture of nitric and sulphuric acids, *dinitrobenzylsulphonic acid*, $C_6H_3(NO_2)_2CH_2.SO_3H$, is obtained; it forms salts, which crystallize well. On reduction it is converted into *diamidobenzylsulphonic acid*, $C_6H_3(NH_2)_2CH_2.SO_3H$, which crystallizes from hot water in silky needles.[2]

SELENIUM COMPOUNDS OF BENZYL.

2074 *Benzyl selenide*, $(C_6H_5.CH_2)_2Se$, is prepared by treating phosphorus pentaselenide with alcoholic soda solution in absence of air, and heating the sodium selenide thus formed with benzyl chloride to the boiling point of the latter. When the solution cools, benzyl selenide separates out first and then some benzyl diselenide, which is separated by recrystallization from hot alcohol. Benzyl selenide crystallizes in long, white needles or transparent prisms, which have a faint aromatic odour and melt at 45·5°. Like methyl selenide, it combines with acids forming unstable salts.

Benzyl diselenide, $(C_6H_5.CH_2)_2Se_2$, is obtained by boiling crude sodium selenide, prepared by igniting sodium selenite with charcoal, with alcohol and benzyl chloride. It crystallizes from hot alcohol in straw-yellow, fatty scales, which melt at 90° and become coloured red in the sunlight. Nitric acid oxidizes it to *benzylselenic acid*, $C_6H_5.CH_2SeO_2H$, crystallizing from hot water in needles which when impure possess a most unpleasant smell, which is not nearly so strong in the pure compound. It is a strong acid.

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[1] v. Pechmann, *Ber. Deutsch. Chem. Ges.* vi. 534.
[2] Mohr, *Ann. Chem. Pharm.* ccxxi. 215.

When benzyldiselenide is digested for some days with methyl iodide, a black mass is obtained which is a mixture of benzyl iodide, trimethylselenine iodide and *benzyldimethylselenine tri-iodide:*

$$(C_6H_5.CH_2)_2\ Se_2 + 5CH_3I =$$
$$C_6H_5.CH_2I + (CH_3)_3SeI + C_6H_5.CH_2(CH_3)_2SeI_3.$$

The latter crystallizes from hot alcohol in black, heavy needles which have a metallic lustre, melt at 65° and possess a repulsive odour. They commence to sublime below 100°, and their vapour attacks the eyes violently. If the alcoholic solution be treated with silver nitrate, the excess of silver removed by hydrochloric acid and the filtrate then treated with platinum chloride, a precipitate of $(C_6H_5.CH_2.(CH_3)_2Se)_2\ PtCl_6$ is obtained consisting of microscopic, yellow, quadratic plates.[1]

NITROGEN BASES OF BENZYL.

THE BENZYLAMINES.

2075 Cannizzaro states in his first paper on the alcohol of benzoic acid, that when the ethereal chloride prepared from it by the action of hydrochloric acid is treated with alcoholic ammonia, a base which differs from toluidine is formed (p. 89). Three years later he found that this is tribenzylamine, $(C_7H_7)_3N$.[2] In the year 1862, Mendius made the important discovery that the nitrils of the fatty acids combine with hydrogen to form amines, and that those of the aromatic series behave in a similar manner, inasmuch as benzonitril, C_7H_5N, yields a powerful base, C_7H_9N, which, however, is not identical with toluidine, "as might have been expected from the hitherto accepted views as to the relations of the bases homologous with aniline to the corresponding members of the benzoic acid series," but differs both from it and the isomeric methylaniline in its properties. It also appeared to him improbable that it was identical with the lutidine contained in coal-tar oil; he, therefore, decided, in the absence of a careful comparison between the two substances, "to introduce the base prepared from benzonitril into scientific literature as a new compound and to denote it by a new name."[1] Two years later, Cannizzaro published a paper on "The Amines of Benzyl Alcohol" in which he says "Toluidine, C_7H_9N, is generally looked upon as the primary benzylamine. I have obtained results which do not agree with this supposition." He found that the primary benzylamine, which he had prepared from benzyl cyanate (benzyl isocyanurate), is a strong base resembling ethylamine and amylamine in its properties. He also obtained it, together with dibenzylamine and tribenzylamine, by heating benzyl chloride with alcoholic ammonia,[2] and described the separation of these bases and the properties of benzylamine.[3] In order to prepare the latter, a mixture of benzyl chloride and alcoholic ammonia is allowed to stand for some days; a portion of the tribenzylamine separates out in crystals, and a further quantity is left behind when the alcohol is removed from the filtrate by distillation and the residue treated with hot water. The solution is then evaporated to dryness, and the most soluble portion of the residue, consisting chiefly of benzylamine hydrochloride is separated by fractional crystallization. This is then decomposed by caustic potash and the base allowed to remain in contact with some solid potash in order to dry it, and at the same time avoid exposure to carbon dioxide. It is then purified as much as possible by fractional distillation and treated with dry carbon dioxide; a solid compound is formed which is washed with anhydrous ether to remove the last adhering traces of dibenzylamine. The residue is then converted into the crystallized hydrochloride and the pure base finally liberated by caustic potash.

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[1] Loring Jackson, *Ann. Chem. Pharm.* clxxix. 8.
[2] *Jahresb.* 1856, 582.

According to Limpricht, the base is prepared by heating benzyl chloride with a solution of ammonia in commercial absolute alcohol for twenty-four hours in a steam bath and removing free ammonia and the largest portion of the alcohol by distillation. The residue is treated with water to precipitate the mixed bases, which are then dissolved in alcohol and treated with hydrochloric acid, the acid solution being allowed to cool gradually. Tribenzylamine hydrochloride separates out in prisms or needles, and a mixture of this salt with plates of dibenzylamine hydrochloride is obtained by the concentration of the mother-liquor; the residual liquid after repeated evaporation to a syrup, solution in hot water and reconcentration, yields benzylamine hydrochloride. The water employed for the precipitation of the bases contains some benzylamine, which may be extracted by saturating the liquid with hydrochloric acid, evaporating to dryness and extracting with hot absolute alcohol, which leaves ammonium chloride undissolved. The hydrochlorides of di- and tri-benzylamine are purified by re-crystallization from water or alcohol.

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[1] *Ann. Chem. Pharm.* cxxi. 144. [2] *Ibid.* cxxxiv. 128. [3] *Ibid.* Suppl. iv. 24.

The primary base is always present in the smallest quantity, while the relative amounts of the other two are very variable; sometimes a large quantity of tribenzylamine is formed with only traces of dibenzylamine, while in other cases the relation is the inverse of this.[1]

2076 *Benzylamine*, $C_6H_5.CH_2.NH_2$. Mendius obtained this compound by treating benzonitril in alcoholic solution with zinc and hydrochloric acid, freeing the solution from alcohol and unattacked nitril by distillation, saturating the residue with caustic potash and extracting the benzylamine with ether. The ethereal solution is then treated with hydrochloric acid, the benzylamine hydrochloride, which is obtained on evaporating the solution, re-crystallized from absolute alcohol and the pure base then set free by caustic potash.

Hofmann obtained benzylamine by the action of zinc and hydrochloric acid on thiobenzamide, $C_6H_5.CS.NH_2$,[2] which is formed by the direct combination of sulphuretted hydrogen with benzonitril:

$$C_6H_5.CS.NH_2 + 4H = C_6H_5.CH_2.NH_2 + H_2S.$$

Both these methods are tedious, and, like the preparation from benzyl chloride and ammonia, only give a small yield. Benzylamine can, however, be readily prepared in large quantities by heating benzyl chloride with an equivalent amount of silver cyanate, until the violent reaction has ceased; a mixture of benzyl isocyanate and benzyl isocyanurate is formed and after distillation is re-distilled over caustic potash. The product thus obtained contains some di- and tri-benzylamine, since the mixture of isocyanates always contains some benzyl chloride. These can be removed by converting the whole into the hydrochlorides or by extracting the benzylamine by shaking out with water.

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[1] *Ann. Chem. Pharm.* cxliv. 304.
[2] *Ber. Deutsch. Chem. Ges.* i. 102.

It is then converted into the hydrochloride which is decomposed by caustic potash, and the base dried over solid potash and redistilled.[1]

It can also be readily obtained by decomposing benzylacetamide, $C_6H_5.CH_2.NH.(C_2H_3O)$, which is prepared by the action of benzyl chloride on acetamide, with alcoholic potash.[2]

Another simple method of preparation has been found by Hofmann. On heating benzyl chloride with potassium cyanide, phenylacetonitril, $C_6H_5.CH_2.CN$, is obtained; when water is added to a solution of this compound in concentrated sulphuric acid, phenylacetamide, $C_6H_5.CH_2.CO.NH_2$ is precipitated. This is then treated with a molecule of bromine, a 5 per cent. solution of four molecules of caustic potash added with continual agitation and the liquid heated by a current of steam: a mixture of benzylamine and brominated benzylamine distils over, which is converted into pure benzylamine when allowed to stand for some time over sodium amalgam, all the bromine being replaced by hydrogen.[3]

Hofmann has shown that the amides of other monobasic acids can readily be converted by this reaction into amines containing one atom of carbon less in the molecule. He has carefully investigated the course of the reaction in the case of acetamide, and finds that acetbromamide, $CH_3.CO.NHBr$, is first formed, and that this loses hydrobromic acid with formation of methyl isocyanate, which assumes the elements of water and splits up into carbon dioxide and methylamine.

Benzaldehyde, which is now a cheap commercial product, can also be readily converted into benzylamine. It combines with hydrocyanic acid to form phenylhydroxyacetonitril, $C_6H_5.CH(OH_2)CN$, which is converted by treatment with alcoholic ammonia into phenylamido-acetonitril, $C_6H_5.CH(NH_2)CN$. On boiling this with dilute sulphuric acid, phenylamido-acetic acid is formed and decomposes into benzylamine and carbon dioxide on distillation. These products of decomposition recombine to some extent forming benzylammonium benzylcarbamate (p. 114), which is, however, readily decomposed by alkalis. Pure benzylamine hydrochloride may also be obtained by treating the distillate with hydrochloric acid.[4]

Properties.—Benzylamine is a colourless liquid which has a characteristic, faint, aromatic odour, does not become coloured in the light, boils at 185° and has a sp. gr. of 0·990 at 14°. It is soluble in water in every proportion, but is insoluble in strong alkalis, and is therefore precipitated by caustic potash from its aqueous solution. It has a strong alkaline reaction, fumes with hydrochloric acid and rapidly absorbs carbon dioxide, so that a drop exposed to the air is soon converted into small, silky needles of the carbonate. It combines with benzyl chloride to form dibenzylamine hydrochloride.

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[1] Strakosch, *Ber. Deutsch. Chem. Ges.* v. 692.

[2] Rudolph, *ibid.* xii. 1297.

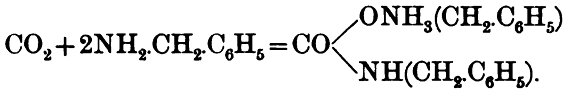
[3] *Ibid.* xviii. 2734.

[4] Friedländer and Tiemann, *ibid.* xiv. 1969.

Benzylamine hydrochloride, $C_7H_7NH_3Cl$, forms quadratic tablets, very soluble in water and alcohol; its platinichloride is a granular, crystalline precipitate.

Benzylamine nitrite, $C_7H_7NH_3.NO_2$, is obtained by shaking the hydrochloride with silver nitrite and ether. It is extracted from the silver chloride, which is simultaneously formed, by cold absolute alcohol, and is deposited on the evaporation of this solution in well-formed crystals, which decompose with evolution of nitrogen when gently warmed.[1]

Benzylammonium benzylcarbamate is formed by the combination of benzylamine with carbon dioxide:



$$CO_2 + 2NH_2.CH_2.C_6H_5 = CO\left\langle\begin{matrix} ONH_3(CH_2.C_6H_5) \\ NH(CH_2.C_6H_5). \end{matrix}\right.$$

It is readily soluble in water, volatilizes when the solution is boiled, and crystallizes from alcohol in small, lustrous plates which melt at 99°.

2077 *Dibenzylamine,* $(C_6H_5.CH_2)_2NH$, is a thick liquid, which has a sp. gr. of 1·033 at 14° and is insoluble in water, but readily soluble in alcohol. When a small quantity is rapidly heated it distils unaltered at above 300°, but on gradual distillation it is decomposed with formation of ammonia, toluene, dibenzyl, $C_{14}H_{14}$, stilbene, $C_{14}H_{12}$, lophine, $C_{21}H_{16}N_2$, and other bodies.[2] When heated to 260° in a stream of hydrochloric acid, it gradually and incompletely decomposes into benzyl chloride and benzylamine hydrochloride, while at 100° it combines with benzyl chloride forming tribenzylamine. On treatment with bromine and a large quantity of water, it decomposes into benzylamine and benzaldehyde:

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[1] Curtius, *Ber. Deutsch. Chem. Ges.* xvii. 958.

[2] Brunner, *Ann. Chem. Pharm.* cli. 131.

$$(C_6H_5.CH_2)_2NH+H_2O+Br_2=$$
$$C_6H_5.COH+C_6H_5.CH_2.NH_2+2HBr.$$

Iodine has a similar action but requires a temperature of 140° (Limpricht).

Dibenzylamine hydrochloride, $(C_7H_7)_2NH_2Cl$, is readily soluble in hot water and alcohol, but much less freely in the cold, and crystallizes in large, flat, prisms, or, when its alcoholic solution is rapidly cooled, in thin plates. The hydrobromide and hydriodide are very similar.

Dibenzylamine nitrate, $(C_7H_7)_2NH_2.NO_3$, is less soluble than the other salts and crystallizes in flat needles or prisms.

Tribenzylamine, $(C_6H_5.CH_2)_3N$, is also formed, together with other bodies, when benzaldehyde is gradually heated to 180° with ammonium formate. Formamide is the first product and decomposes into carbonic oxide and ammonia, which then act upon the benzaldehyde:

$$3C_6H_5.COH+3CO+NH_3=(C_6H_5.CH_2)_3N+3CO_2.$$

This is the most convenient method for the preparation of tribenzylamine, 100 grms. of benzaldehyde yielding 40 grms. of the pure product.[1] It is slightly soluble in cold alcohol and crystallizes from a hot solution in needles, plates, or monoclinic tablets (Panebianco) melting at 91°. Small quantities can be distilled without decomposition, but larger quantities split up, yielding the same products as the secondary base. It also resembles the latter in its behaviour towards bromine and iodine, benzaldehyde and dibenzylamine being formed. When its hydrochloride is heated to 250° in a stream of hydrochloric acid, it decomposes into benzyl chloride and dibenzylamine hydrochloride, while Lauth obtained benzyl chloride and ammonium chloride by treating the free base in a similar manner at 180°[2]. It does not combine with benzyl chloride, and hence no tetrabenzylammonium chloride is formed in its preparation from benzyl chloride and ammonia; it combines with ethyl iodide, however, on heating to form a crystallized compound, which does not yield a hydroxide on treatment with silver oxide, but decomposes into its constituents.[3] It also forms a crystallized compound when heated with methyl sulphate to 100°.[1]

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[1] Leuckart, *Ber. Deutsch. Chem. Ges.* xviii. 2341.

[2] *Ibid.* vi. 678.

[3] Vasca-Lanza, *ibid.* vii. 82.

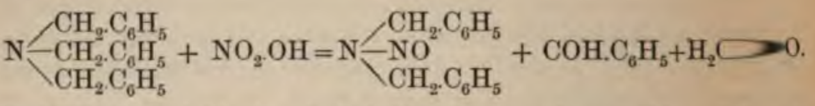
The salts of tribenzylamine have been crystallographically investigated by Panebianco.[2]

Tribenzylamine hydrochloride, $(C_7H_7)_3NHCl$, is slightly soluble in cold alcohol and water, and crystallizes from its hot solution in quadratic prisms. It decomposes above 270°, a large quantity of toluene being formed (Rohde). The platinichloride crystallizes in orange-coloured, monoclinic needles.

Tribenzylamine nitrate, $(C_7H_7)_3NHNO_3$, forms rhombic crystals which are insoluble in water and slightly soluble in alcohol.

Tribenzylamine sulphate, $((C_7H_7)_3NH)_2SO_4$, forms monoclinic crystals, is insoluble in water, slightly soluble in alcohol, and combines with aluminium sulphate forming tribenzylammonium alum, $(C_{21}H_{22}N)_2Al_2(SO_4)_4 + 24H_2O$, which is deposited in regular crystals and is soluble in water but not in alcohol.

Nitrosodibenzylamine, $(C_7H_7)_2N(NO)$. Rohde obtained this compound, together with benzaldehyde, by distilling a concentrated alcoholic solution of tribenzylamine with nitric acid:



$$N\begin{cases}CH_2.C_6H_5\\CH_2.C_6H_5\\CH_2.C_6H_5\end{cases} + NO_2.OH = N\begin{cases}CH_2.C_6H_5\\NO\\CH_2.C_6H_5\end{cases} + COH.C_6H_5 + H_2O.$$

It is readily soluble in alcohol and ether, and crystallizes in quadratic tablets, melting at 52°; it does not combine with acids, and is converted into dibenzylamine by the action of nascent hydrogen or hydrochloric acid.

AMIDO-SUBSTITUTED BENZYLAMINES.

2078 *Diethylbenzylamine*, $C_6H_5.CH_2.N(C_2H_5)_2$, is obtained by heating benzylamine with ethyl iodide, or benzyl chloride with diethylamine. It is a transparent, oily liquid, which boils at 211°—212°, and combines with ethyl iodide on heating with formation of *triethylbenzylammonium iodide*, $N(C_6H_5.CH_2)(C_2H_5)_3I$, which can also be prepared from benzyl iodide and triethylamine, and forms large, colourless crystals, which are readily soluble in water; on dry distillation it is decomposed into triethylamine and benzyl iodide, while it is not attacked when heated with concentrated hydriodic acid.[1] When iodine is added to it in alcoholic solution, the periodide, $N(C_6H_5.CH_2)(C_2H_5)_3I_3$, separates out in black-blue monoclinic prisms, which have a metallic lustre.

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[1] Claesson and Lundvall, *Ber. Deutsch. Chem. Ges*xiii. 1703.

[2] *Jahresb.* 1878, 476.

Ethyldibenzylamine, $(C_6H_5.CH_2)_2NC_2H_5$, was obtained by Limpricht from ethyl iodide and dibenzylamine; it is an oily liquid.

Diethyldibenzylammonium iodide, $(C_6H_5.CH_2)_2(C_2H_5)_2NI$, is formed by the combination of diethylbenzylamine with benzyl iodide. It crystallizes from hot water in needles possessing a diamond lustre; when it is distilled with hydriodic acid, benzyl iodide is liberated (V. Meyer).

Benzylphenylamine, or *Benzylaniline*, $C_6H_5.CH_2.N(C_6H_5)H$, is formed when benzyl chloride is heated with aniline to 160°. The free base crystallizes from hot alcohol in four-sided prisms, melting at 32°.[2] It may also be obtained by the action of hydrochloric acid and zinc-dust on thiobenzanilide,[3] $C_6H_5.CS.N(C_6H_5)H$.

Benzylphenyldimethylammonium chloride, $(C_6H_5.CH_2)C_6H_5(CH_3)_2NCl$, is readily formed by the direct combination of benzyl chloride with dimethylaniline. It crystallizes from water or alcohol in tablets, which melt at 110°, and is split up into its constituents by distillation. It is not decomposed by boiling with water and silver oxide, but its decomposition may be effected by employing silver sulphate. If the sulphuric acid be removed by baryta water from the solution thus formed, and the filtrate concentrated, the hydroxide is obtained as a strongly alkaline, syrupy mass, which is converted into the carbonate in the air. On distillation it decomposes smoothly into dimethylaniline and benzyl alcohol,[4] while tetra-ethylammonium hydroxide under similar conditions yields triethylamine, ethylene and water.

Benzyldiphenylamine, $C_6H_5.CH_2.N(C_6H_5)_2$, is formed when diphenylbenzothiamide, $C_6H_5.CS.N(C_6H_5)_2$, is treated with hydrochloric acid and zinc-dust. It crystallizes from hot alcohol in long white needles which melt at 87°, and does not combine with acids (Bernthsen and Trompetter).

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[1] Ladenburg and Struve, *Ber. Deutsch. Chem. Ges.* x. 43; Ladenburg, *ibid.* x. 561, 1153, 1634; V. Meyer, *ibid.* x. 309, 964, 1291.

[2] Fleischer, *Ann. Chem. Pharm.* cxxxviii, 22.

[3] Bernthsen and Trompetter, *Ber. Deutsch. Chem. Ges.* xi. 1760.

[4] Michler and Gradmann, *ibid.* x. 2079.

Dibenzyltolylamine, $(C_6H_5.CH_2)_2NC_6H_4.CH_3$. This base, which is also known as *dibenzyltoluidine*, was prepared by Cannizzaro by heating paratoluidine with alcohol and benzyl chloride. It crystallizes from hot alcohol in very fine needles, melting at 54·5°—55°, and is a weak base; it differs from the isomeric tribenzylamine in forming salts which are decomposed by water.[1]

SUBSTITUTION PRODUCTS OF THE BENZYLAMINES.

2079 These are formed by the action of ammonia on the corresponding haloid ethers.

Halogen substitution products. These compounds are strong bases and form crystalline salts; the primary compounds absorb carbon dioxide from the air.

			Melting-point.
Parachloro-benzylamine,[2]	$C_6H_4Cl.CH_2.NH_2$,	liquid . .	—
Paradichloro-benzylamine,[3]	$(C_6H_4Cl.CH_2)_2NH$,	crystals . .	29°
Paratrichloro-benzylamine,[4]	$(C_6H_4Cl.CH_2)_3N$,	rhombic prisms	78·5°
Paratribromo-benzylamine,[5]	$(C_6H_4Br.CH_2)_3N$,	prisms . .	78°—79°
Para-iodo-benzylamine,[6]	$C_6H_4I.CH_2.NH_2$,	liquid . .	—
Paradi-iodo benzylamine,[7]	$(C_6H_4I.CH_2)_2NH$,	needles . .	76°
Paratri-iodo-benzylamine,[8]	$(C_6H_4I.CH_2)_3N$,	needles . .	114·5°
Orthobromo-benzylamine,[9]	$C_6H_4Br.CH_2.NH_2$,	liquid . .	—

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[1] *Ann. Chem. Pharm.* Suppl. iv. 80.

[2] Berlin, *Ann. Chem. Pharm.* Suppl. cli. 137; Jackson and Field, *Amer Chem. Journ.* ii. 95.

[3] *Ibid.*

[4] *Ibid.*

[5] Jackson and Lowry, *Ber. Deutsch. Chem. Ges.* x. 1211.

[6] Jackson and Mabery, *Amer. Chem. Journ.* ii. 257.

[7] *Ber. Deutsch. Chem. Ges.* xi. 58.

[8] *Ibid.*

[9] Jackson and White, *Amer. Chem. Journ.* ii. 317.

			Melting-point.
Orthodibromobenzylamine,[1]	$(C_6H_4Br.CH_2)_2NH$	rhombic crystals	36°
Orthotribromobenzylamine,[2]	$(C_6H_4Br.CH_2)_3N$,	crystals . .	121·5°—122°

Paranitrobenzylamines have been prepared by Strakosch by heating paranitrobenzyl chloride with aqueous ammonia to 100°. The primary base could not be isolated; the secondary base combines with acids, while the tertiary does not, thus rendering the separation of these two a matter of no difficulty.[3]

Paradinitrobenzylamine, $(C_6H_4(NO_2)CH_2)_2NH$, crystallizes from hot alcohol in large, yellowish, lustrous plates, melting at 93°; its hydrochloride forms lustrous, yellow prisms, which are only slightly soluble in water and alcohol, while its platinichloride, which crystallizes in yellow needles, is almost insoluble.

Paratrinitrobenzylamine, $(C_6H_4(NO_2)CH_2)_3N$, is slightly soluble in hot alcohol, readily in glacial acetic acid and nitrobenzene, and crystallizes in lustrous, white needles, which melt at 163°, and possess a pleasant odour.

Paranitrobenzylphenylamine, $C_6H_4(NO_2)CH_2.N(C_6H_5)H$, is formed by heating paranitrobenzyl chloride with aniline; it crystallizes from hot alcohol in pointed, lustrous, yellow needles. Its hydrochloride crystallizes from hot hydrochloric acid in small lustrous plates which are decomposed by water with separation of the base (Strakosch).

Metanitrobenzylamines. Aqueous ammonia converts metanitrobenzyl chloride into the secondary and tertiary amines, while in the presence of alcohol only the former, together with a small quantity of the primary base, is formed.[4]

Metanitrobenzylamine, $C_6H_4(NO_2)CH_2.NH_2$, is a yellow, oily liquid, which becomes solid in the air from absorption of carbon dioxide. Its oxalate crystallizes in needles, which are only slightly soluble in water.

Metadinitrobenzylamine crystallizes from alcohol in small yellow, rhombic plates, melting at 87°. Its hydrochloride and platinichloride are only slightly soluble in water.

Metatrinitrobenzylamine is slightly soluble in alcohol, more readily in benzene, and forms monoclinic prisms, melting at 162°. It does not combine with hydrochloric acid.

Metanitrobenzylphenylamine is formed by the action of aniline on metanitrobenzyl chloride. The hydrochloride, which is thus obtained, forms small white, lustrous plates. It is decomposed by water with formation of the base, which crystallizes in long, orange-red needles, melting at 86°.

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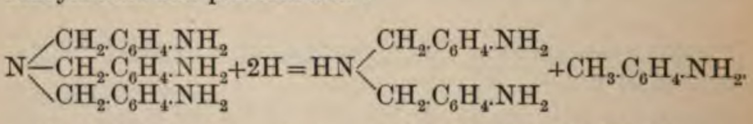
[1] Jackson and White, *Amer. Chem. Journ.* ii. 317.
[2] *Ibid.*
[3] *Ber. Deutsch. Chem. Ges.* vi. 1056.
[4] Borgmann, *Chem. Centralb.* 1885, 456.

Amidobenzylamines are obtained by the reduction of the nitro-compounds with tin and hydrochloric acid.

Paradiamidobenzylamine, $(C_6H_4(NH_2)CH_2)_2NH$, is readily soluble in hot water and alcohol; it crystallizes in needles with a satin lustre, or in plates which melt at 106°, and volatilize without decomposition when more strongly heated. The hydrochloride, $(C_6H_4(NH_3Cl)CH_2)_2NH_2Cl$, is readily soluble in water, slightly in hydrochloric acid, and crystallizes in small white, lustrous plates; the platinichloride, $C_{14}H_{18}N_3Cl.PtCl_6$, forms large pointed reddish-yellow needles which are readily soluble in water.

Paratriamidobenzylamine, $(C_6H_4(NH_2)CH_2)_3N$, is insoluble in water, and crystallizes from hot alcohol in octahedra, possessing a diamond lustre and melting at 136°. Its hydrochloride crystallizes in yellow needles, and is so readily soluble in water, alcohol, and hydrochloric acid, that it cannot be obtained pure.

In the preparation of the base, the action of the tin and hydrochloric acid must not be allowed to continue too long, as under these circumstances it is split up into paradiamidobenzylamine and paratoluidine:



$$N\left\langle\begin{array}{l}CH_2.C_6H_4.NH_2\\CH_2.C_6H_4.NH_2\\CH_2.C_6H_4.NH_2\end{array}\right.+2H=HN\left\langle\begin{array}{l}CH_2.C_6H_4.NH_2\\CH_2.C_6H_4.NH_2\end{array}\right.+CH_3.C_6H_4.NH_2.$$

Paramidobenzylphenylamine, $C_6H_4(NH_2)CH_2.N(C_6H_5)H$, cannot be obtained by the action of tin and hydrochloric acid on the nitro-compound, since a more deeply seated decomposition takes place; the reduction may, however, be effected by employing ammonium sulphide. The base is soluble in water and alcohol, and crystallizes in silky scales, which melt at 88° and become coloured red in the light.

Metadiamidobenzylamine forms prismatic needles, melting at 86°; its hydrochloride, $(C_6H_4(NH_3Cl)CH_2)_2NH_2Cl$, crystallizes from concentrated hydrochloric acid in long, pinkish needles, and forms a readily soluble platinichloride.

Metatriamidobenzylamine forms needles melting at 142°; its platinichloride is only slightly soluble.

Metamidobenzylphenylamine melts at 67°.

BENZYL-DERIVATIVES OF THE ACID-AMIDES AND ALLIED BODIES.

2080 *Benzylacetamide*, $C_6H_5.CH_2.N(C_2H_3O)H$, was prepared by Strakosch by heating benzylamine with glacial acetic acid for several hours;[1] it is more readily formed by the action of benzyl chloride on acetamide,[2] and is very soluble in alcohol and ether, slightly in petroleum naphtha, from which it crystallizes in small plates, which have a pleasant smell of flowers and melt at 57°. It boils at 300° and is not attacked by acids or aqueous alkalis; alcoholic potash, however, converts it into acetic acid and benzylamine.

Dibenzyloxamide, $(C_6H_5.CH_2.NH_2)_2C_2O_2$, is obtained by boiling benzylamine with ethyl oxalate; it is insoluble in water, slightly soluble in hot alcohol, from which it crystallizes in scales, which possess a satin lustre and melt at 216°.

Cyanobenzylamine, $C_{18}H_{16}N_4$, is obtained by passing cyanogen into a cold solution of benzylamine:

$$\begin{array}{l}C_6H_5.CH_2.NH_2\\ \\ C_6H_5.CH_2.NH_2\end{array} + \begin{array}{c}C{\equiv}N\\ |\\ C{\equiv}N\end{array} = \begin{array}{r}C_6H_5.CH_2.NH.C{=}NH\\ |\\ C_6H_5.CH_2.NH.C{=}NH.\end{array}$$

It forms lustrous crystals, which are soluble in alcohol and melt at 140°. If hydrochloric acid be added to the alcoholic solution, the salt, $C_{18}H_{16}N_4(ClH)_2$, is obtained in white, silky needles. When it is allowed to stand in contact with hydrochloric acid for some time, it is converted into dibenzyloxamide (Strakosch).

Benzylcyanamide, $C_6H_5.CH_2.NH(CN)$, is formed when cyanogen chloride is passed into an ethereal solution of benzylamine, and crystallizes in tablets melting at 33°. It changes spontaneously into *benzylcyanuramide* or *benzylmelamine*, $(C_6H_5.CH_2.NH)_3C_3N_3$, which has a much higher melting-point and crystallizes from alcohol in plates; the change takes place more readily at 100°.

When an alcoholic solution of benzylcyanamide is boiled with benzylamine hydrochloride, *dibenzylguanidine* $(C_6H_5.CH_2.NH)_2C.NH$, is formed; this compound crystallizes from alcohol in plates or tablets, melting at 100°. The hydrochloride, $(C_7H_7.NH)_2C.NH.ClH$, is slightly soluble in water, more readily in alcohol (Strakosch).

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[1] *Ber. Deutsch. Chem. Ges.* v. 697.

[2] Rudolph, *ibid.* xii. 1297.

Dibenzylcyanamide, $(C_6H_5.CH_2)_2N.CN$, was obtained by Limpricht from dibenzylamine and cyanogen chloride; it crystallizes from alcohol in plates, melting at 53°—54°.

Benzyl isocyanate, or *Benzyl carbimide*, $C_6H_5.CH_2N:CO$, was prepared by Letts in the impure state and in small quantity, by distilling benzyl chloride with silver cyanate;[1] the isocyanurate is always formed at the same time. It is a liquid which gives all the characteristic reactions of the isocyanates and possesses an extremely penetrating odour, its vapour attacking the eyes violently.

Benzyl isocyanurate, $(C_6H_5.CH_2)_3N_3(CO)_3$, crystallizes from hot alcohol in silky needles, melting at 157°. It boils above 320°, and when fused with caustic potash yields benzylamine. Cannizzaro seems to have obtained the same substance in small quantity and together with other products by the action of cyanuric chloride on benzyl alcohol.[2]

Benzyl isothiocyanate, or *Benzyl mustard oil*, $C_6H_5.CH_2.N:CS$. Hofmann obtained this compound by dissolving benzylamine in carbon disulphide, and distilling the white, crystalline compound formed with an alcoholic solution of mercuric chloride.[3]

It is a liquid which boils at about 243° and possesses the smell of water-cress (*Nasturtium officinale*) in such a remarkable degree that Hofmann was induced to search for it in the oil of this plant; it is not, however, present, the odoriferous constituent in water-cress being phenylpropionitril, $C_6H_5.C_2H_4.CN$,[4] while benzonitril, C_6H_5CN, is that of the nasturtium (*Tropaeolum majus.*)[5]

Benzyl thiocyanate, $C_6H_5.CH_2.S.CN$, is formed by heating benzyl chloride with an alcoholic solution of potassium thiocyanate. It is insoluble in water, and crystallizes from alcohol in long, transparent prisms, which have a sharp, burning taste, and a penetrating smell resembling that of cress. According to Henry,[6] it melts at 36°—38° and boils with partial decomposition at 256°, while Barbaglia found its melting-point to be 41° and its boiling-point 230°—235°.[7]

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[1] *Ber. Deutsch. Chem. Ges.* v. 90; see also Strakosch, *ibid.* v. 692; Ladenburg, *ibid.* x. 46.

[2] *Ber. Deutsch. Chem. Ges.* iii. 517.

[3] *Ibid.* i. 201.

[4] *Ibid.* vii. 520.

[5] *Ibid.* vii. 518.

[6] *Ibid.* ii. 638.

[7] *Ibid.* v. 688.

Concentrated nitric acid converts it into *paranitrobenzyl thiocyanate*, $C_6H_4(NO_2)CH_2S.CN$, which can also be obtained by the action of paranitrobenzyl chloride on potassium thiocyanate. It crystallizes from alcoholic solution in small, brittle crystals.

Various halogen substitution-products of this compound are also known.[1]

Benzyl selenocyanate, $C_6H_5.CH_2.Se.CN$, crystallizes from alcohol in white needles or prisms, which have an extremely repulsive smell and melt at 71·5°.[2]

Benzyl carbamate, or *Benzyl urethane*, $C_6H_5.CH_2.O.CO.NH_2$, was obtained by Cannizzaro, together with a little benzyl isocyanurate and dibenzyl urea, by the action of cyanogen chloride and cyanuric chloride on benzyl alcohol.[3] It is also formed when urea nitrate is heated to 130°—140°[4] with benzyl alcohol; it crystallizes from hot water in large plates, which melt at 86° and decompose into benzyl alcohol and cyanuric acid at 220°.

Benzyl urea, $(C_6H_5.CH_2)NH.CO.NH_2$, is formed, together with symmetric dibenzyl urea, by the action of benzyl chloride on an alcoholic solution of potassium cyanate,[5] as well as by that of alcoholic ammonia on benzyl isocyanate (Letts). It is also obtained when a solution of benzylamine hydrochloride is boiled with potassium cyanate.[6] It is tolerably soluble in hot, readily in boiling alcohol, and crystallizes in long, white needles, melting at 147°—147·5°.

Symmetric dibenzyl urea, $CO(NH.CH_2.C_6H_5)_2$, is formed when the compound just described is heated to 200° (Cannizzaro), as well as when benzyl isocyanate is heated with water in a sealed tube to 100°, and also when benzyl alcohol is heated to 100° with urea nitrate (Letts), benzylaldehyde being simultaneously formed (Campisi and Amato). It is insoluble in water and crystallizes from alcohol in needles melting at 167°. It does not combine with hydrochloric acid or nitric acid, but gives a plantinichloride.

Asymmetric dibenzyl urea, $(C_6H_5.CH_2)_2N.CO.NH_2$, has been obtained by Paternò and Spica from dibenzylamine hydrochloride and potassium cyanate; it is slightly soluble in cold, readily in hot water, and crystallizes in thick prisms, melting at 124°—125°.

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[1] Jackson, Field, Mabery, Lowry, *loc. cit.*

[2] Jackson, *Ann. Chem. Pharm.* clxxix. 15.

[3] *Ber. Deutsch. Chem. Ges.* iii. 517 ; iv. 412.

[4] Campisi and Amato, *ibid.* iv. 412.

[5] Paternò and Spica, *ibid.* ix. 81.

[6] *Ibid.*

Benzyl thiocarbamide, $C_6H_5.CH_2.NH.CS.NH_2$, has been prepared in an analogous manner from benzylamine hydrochloride and potassium thiocyanate; it is very soluble in water and melts at 101°.

Symmetric dibenzyl thiocarbamide, $(C_6H_5.CH_2.NH)_2CS$, is formed when an alcoholic solution of benzylamine is heated with carbon disulphide until the evolution of sulphuretted hydrogen ceases. It crystallizes in large, four-sided, lustrous tablets, melting at 114°; it is converted into dibenzyl urea when its alcoholic solution is treated with mercuric oxide (Strakosch).

Asymmetric dibenzyl thiocarbamide, $(C_6H_5.CH_2N)_2CS.NH_2$, is prepared from dibenzylamine hydrochloride and potassium thiocyanate; it is slightly soluble in water, readily in alcohol, and crystallizes in long needles melting at 156°—157° (Paternò and Spica).

PHOSPHORUS COMPOUNDS OF BENZYL.

2081 Primary and secondary benzylphosphine are formed when benzyl chloride is heated with phosphonium iodide and zinc oxide. The product of the reaction is distilled with water, an oily liquid coming over, which possesses a very characteristic, persistent odour, and is a mixture of toluene and benzylphosphine. The residue contains dibenzylphosphine and other substances, which, however, remain in solution, while the dibenzylphosphine crystallizes out on standing, more rapidly in the presence of caustic potash; it is then removed from the liquid and recrystallized from boiling alcohol.[1]

Benzylphosphine, $C_6H_5.CH_2.PH_2$, is a strongly refractive liquid, boiling at 180°; it is oxidized on exposure to the air with such rapidity that its temperature rises to above 100°, thick, white needles being deposited.

Benzylphosphonium iodide, $C_6H_5.CH_2.PH_3I$, is obtained by the addition of fuming hydriodic acid to benzylphosphine, as a white precipitate which crystallizes from the hot acid in long, white needles. When these are washed with ether and dried in a stream of hydrogen, they are converted into large, well-formed tablets. Water decomposes the compound into its constituents.

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[1] Hofmann, *Ber. Deutsch. Chem. Ges.* v. 100.

Dibenzylphosphine, $(C_6H_5CH_2)_2PH$, crystallizes in needles which form star-like aggregates, are colourless and tasteless, do not combine with acids, and melt at 205°. While dimethylphosphine and ethylphosphine are spontaneously inflammable in the air, dibenzylphosphine is not acted upon by oxygen, even at a higher temperature.

Triphenylbenzylphosphonium chloride, $P(C_6H_5)_3(CH_2.C_6H_5)Cl$, is readily formed by the combination of benzylchloride with triphenylphosphine. It is readily soluble in alcohol and water, and separates from the latter in rhombic crystals which contain one molecule of water and are efflorescent. Other salts, which are characterized by their power of crystallization, have been prepared from this compound by double decomposition; they are decomposed by boiling caustic soda, with formation of triphenylphosphine oxide and toluene:[1]

$$P(C_6H_5)_3(C_6H_5.CH_2)Cl+NaOH=PO(C_6H_5)_3+C_6H_5.CH_3+NaCl.$$

ARSENIC COMPOUNDS OF BENZYL.

2082 When benzyl chloride, diluted with absolute ether, is treated with arsenic trichloride and sodium, a reaction commences after some time, which in the course of a few days may raise the temperature to the boiling-point of ether, the following compounds being formed:

$$2C_7H_7Cl+AsCl_3+2Na=\overset{\text{Dibenzylarsine trichloride.}}{(C_7H_7)_2AsCl_3}+2NaCl.$$

$$3C_7H_7Cl+AsCl_3+4Na=\overset{\text{Tribenzylarsine dichloride.}}{(C_7H_7)_3AsCl_2}+4NaCl.$$

If the sodium chloride be now removed, the ether distilled off and the residue treated with ordinary ether containing water, the chlorides are converted into oxychlorides, which separate out as a powder, while resinous by-products containing arsenic go into solution. The powder is washed with ether and then treated with boiling dilute caustic soda solution; dibenzylarsenic acid goes into solution, while the residue consists of tribenzylarsine oxide, which is very slightly soluble in the cold solution, and is, therefore, removed by cooling and filtering.

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[1] Michaelis and V. Soden, *Ann. Chem. Pharm.* ccxxix. 319.

Dibenzylarsenic acid, $(C_6H_5.CH_2)_2AsO.OH$, is precipitated from its alkaline solution by acids; it is only very slightly soluble in cold, more readily in boiling water, and crystallizes from hot dilute alcohol in fine, white plates, melting at 210·5°. It dissolves in hot dilute hydrochloric acid and the solution on cooling deposits the compound $(C_7H_7)_2As(OH)_2Cl$, in fine needles, which melt at 128° and are reconverted into the acid by water. It forms similar compounds with hydrobromic, hydriodic and nitric acids. It is decomposed on heating with concentrated hydrochloric acid:

$$2(C_7H_7)_2AsO_2H + 2HCl = 2C_7H_7Cl + 2C_7H_8 + As_2O_3 + H_2O.$$

It behaves in this reaction similarly to cacodylic or dimethylarsenic acid. Its alkaline salts are soluble in water and alcohol; those of the calcium group separate from alcohol in crystals; the silver salt is a white precipitate, insoluble in water.

Tribenzylarsine oxide, $(C_6H_5.CH_2)_3AsO$, crystallizes from dilute alcohol in lustrous needles, melting at 219·5°. On heating with hydrochloric acid it is converted into the oxychloride, $(C_7H_7)_3As(OH)Cl$, which melts at 162°—163° and is reconverted into the oxide by alkalis.

Tribenzylarsine, $(C_6H_5CH_2)_3As$. When a little acetic ether is added to the mixture employed in the preparation of the compounds just described, the reaction becomes so violent that it has to be moderated by cooling:

$$3C_7H_7Cl + AsCl_3 + 6Na = (C_7H_7)_3As + 6NaCl.$$

If the treatment described above be then proceeded with, the oxychlorides are obtained as before, but the solution contains tribenzylarsine and no resinous by-products; it crystallizes from alcohol in large colourless needles, melting at 104°. On heating with ethyl iodide, *tribenzylarsonium iodide*, $(C_6H_5.CH_2)_3C_2H_5AsI$, is formed, and crystallizes in small white plates, which are slightly soluble in water, readily in alcohol.[1]

Tribenzylarsine is isomeric with tritolylarsine, $(C_6H_4.CH_3)_3As$, which, like triphenylarsine, forms no compounds with the alcoholic iodides.

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[1] Michaelis and Paetow, *Ber. Deutsch. Chem. Ges.* xviii. 41.

SILICON COMPOUNDS OF BENZYL.

2083 *Silicon tetrabenzyl,* or *Silicotetrabenzylmethane,* $Si(CH_2.C_6H_5)_4$, is formed by the action of sodium on a mixture of benzylchloride and silicon chloride, to which a little acetic ether has been added, and which has been diluted with ether. It separates from warm ether in crystals melting at 127·5°.[1]

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[1] Polis, *Ber. Deutsch. Chem. Ges.* xviii. 1543.

THE BENZOYL GROUP.

2084 It has been already mentioned in the introductory sketch of the development of organic chemistry (Part I. p. 11), that Wöhler and Liebig showed in their classical research, *Investigations on the Radical of Benzoic Acid*, that oil of bitter almonds, benzoic acid, and a number of substances prepared from these, all contain a "compound basis" of the formula C_7H_5O, to which they gave the name of benzoyl (the latter portion of the word being derived from ὕλη, matter).[1] They communicated their results to Berzelius, who makes the following remarks in his reply:

"The results which you have obtained by the investigation of oil of bitter almonds, are certainly the most important which have hitherto been attained in the field of vegetable chemistry, and promise to throw an unexpected light upon that department of science. The fact that a substance which is composed of carbon, hydrogen and oxygen, combines with other substances, but especially with those which form salts and bases, in precisely the same manner as do simple substances, proves that there are ternary compound atoms (of the first order), and the radical of benzoic acid is the first well-established instance of a ternary substance which possesses the properties of an element.

"The facts brought forward by you give rise to such wide considerations that they may be looked upon as marking the commencement of a new era in vegetable chemistry. From this standpoint I should propose to name the first discovered radical composed of more than two elements, *proin* (from the word πρωὶ, commencement of the day, in the sense, ἀπὸ πρωὶ ἕως ἑσπέρος, Acts xxviii. 23), or *orthrin* (from ὀρφρός, dawn.)"

In view, however, of the circumstance that the long familiar name benzoic acid would have also been altered, and that it is customary to respect terms in general use, provided only that they do not admit of a double interpretation, it seemed to him most suitable to accept the name benzoyl.[1]

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[1] *Ann. Chem. Pharm.* iii. 249.

In the next year, nevertheless, he opposed the idea of the existence of oxygenated radicals and looked upon oil of bitter almonds as an oxide of *picramyl*, C_7H_6 (πικρός, bitter, and ἀμυγδάλη, almond), a name which was never generally adopted.

BENZALDEHYDE, $C_6H_5.CHO$.

2085 The poisonous qualities of bitter almonds were known to the ancients, and they were employed in medicine in the middle ages: Valerius Cordus, who has been already mentioned under the history of ether, described them as constituents of lozenges. At the commencement of this century, Bohm, an apothecary's assistant in Berlin, discovered that the aqueous distillate of bitter almonds contains prussic acid,[2] and this discovery led to the assumption that the latter is poisonous, a property which its discoverer, Scheele, had, somewhat strangely, overlooked. Schaub, Schrader, Ittner and other chemists[3] confirmed the dangerous nature of this substance, and Schrader,[4] and Matrès,[5] an apothecary in Montauban, observed that a liquid oil is also obtained by the distillation of bitter almonds with water. This oil was more closely examined by Vogel and Robiquet, the former[6] of whom found that the most remarkable and striking property of oil of bitter almonds is that it is converted into a crystalline body by exposure to the air or by treatment with pure oxygen or oxymuriatic acid (chlorine), while Robiquet showed that the leaves of the cherry-laurel yield an oil which resembles oil of bitter almonds in every respect, and that the substance obtained from it by oxidation has acid properties.[7]

Stange, an apothecary of Basel, who also obtained this solid substance from the cherry-laurel, recognized it as benzoic acid,[8] an observation which was confirmed by Wöhler and Liebig. These chemists determined its composition, and that of the oil of bitter almonds, and ascertained the relations of the two compounds. To oil of bitter almonds they gave the name of benzoyl hydride, which was later changed to benzoic aldehyde and benzaldehyde.

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[1] *Ann. Chem. Pharm.* iii. 282.
[2] *Scherer's Journ.* x. 126; Gilbert, *Ann. Phys.* xiii. 503.
[3] Ittner, *Beiträge zur Geschichte der Blausäure*, Freiburg and Constanz, 1809; Preyer, *Die Blausäure*, Bonn, 1870, 154.
[4] Schrader, *Berlin. Jahrb. Pharm.* ii. 43.
[5] *Journ. Pharm.* v. 289.
[6] Schweigger, *Journ. Chem. Phys.* xx. 59; xxxii. 119.
[7] *Ann. Chim. Phys.* xv. 29; xxi. 250.
[8] Buchner's *Repert. Pharm.* xiv. 329, 361; xvi. 80.

Shortly before this, Robiquet and Boutron-Charlard had found that when bitter almonds are freed from fatty matters by pressure, an odourless residue is left which yields the characteristic smell of oil of bitter almonds on the addition of water. The oil in question, or its elements, had therefore been left behind in the pressed mass and had not been removed by the process. They, therefore, concluded that oil of bitter almonds is a compound of water with a peculiar principle, which they endeavoured to isolate. The use of water being impossible, they extracted the pressed almonds with boiling alcohol, and obtained, together with resin and a liquid sugar, a crystalline compound containing nitrogen, to which they gave the name of amygdalin. This compound, to which the taste of bitter almonds is due, gave no smell of bitter almonds when treated with water, nor did either of the two other compounds nor the residue, nor even of a mixture of them all. The prussic acid and oil of bitter almonds had vanished from their hands. They found further, that sweet almonds contain no amygdalin, and that the latter yields benzoic acid when oxidized by nitric acid, while Peligot observed the formation of oil of bitter almonds as an intermediate product in this reaction.

Wöhler and Liebig, who also accurately determined the composition of amygdalin, succeeded in finding the solution of the problem. They showed that both sweet and bitter almonds contain a peculiar nitrogenous substance, emulsin, which converts amygdalin in presence of water into benzaldehyde, prussic acid, and grape sugar:

$$C_{20}H_{27}NO_{11} + 2H_2O = C_7H_6O + CNH + 2C_6H_{12}O_6.$$

The action of the ferment is destroyed by boiling water and by heating with alcohol, so that when dried and powdered bitter almonds are shaken up with boiling water and distilled, none of the liquid oil is obtained, and the same result occurs when, as in

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[1] *Ann. Chim. Phys.* xliv. 352.

Robiquet and Boutron-Charlard's process, they are treated with boiling alcohol.[1]

Amygdalin, which is the first example of a glucoside, a large number of which bodies is now known, occurs in many plants, chiefly the *Amygdalaceæ*, *Drupaceæ* and *Pomaceæ*, which all yield benzaldehyde and prussic acid when distilled with water. The kernel of the peach also yields an oil resembling oil of bitter almonds in every respect,[2] while that obtained from the leaves, flowers, seeds and bark of the cherry, contains both oil of bitter almonds and another oil which has a penetrating, repulsive odour.[3] This subject will be further discussed under Amygdalin.

According to Winkler, the fresh leaves of the cherry-laurel (*Prunus laurocerasus*), the cherry (*Prunus padus*) and the peach, contain a small quantity of free oil of bitter almonds varying in amount with the water present,[4] which can be extracted by ether.

Ittner looked upon oil of bitter almonds as a compound of hydrocyanic acid and an ethereal oil, but Vogel opposed this view, for he had found that it could be easily freed from hydrocyanic acid by treatment with caustic potash or baryta water, or by distillation with mercuric oxide.[5] Since, however, the oil containing hydrocyanic acid is readily converted into the polymeric benzoin, $C_{14}H_{12}O_2$, by caustic potash, Wöhler and Liebig proposed to remove the acid by shaking up with milk of lime and ferrous sulphate, calcium ferrocyanide being formed; a loss of about 10 per cent. is experienced in the process. According to Bertagnini it is better to shake the oil with three or four volumes of acid sodium sulphite, remove the crystals which separate out and wash with alcohol.[6] All the hydrocyanic acid is not removed by this process, and the double sulphite is therefore recrystallized from hot alcohol before being distilled with caustic soda.[7] The oil containing hydrocyanic acid is not simply a mixture of benzaldehyde and hydrocyanic acid, but contains *phenylhydroxyacetonitril*, $C_6H_5.CH(OH)CN$, which, like other cyanhydrins or nitrils of hydroxyacids, readily decomposes into its constituents. Winkler had noticed some time previously that crude oil of bitter almonds is converted by hydrochloric acid into *mandelic acid*

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[1] *Ann. Chem. Pharm.* xxii. 1; Robiquet and Boutron, *ibid.* xxv. 175; Liebig, *ibid.* xxv. 190.

[2] Righini, *ibid.* x. 359; Geissler, *ibid.* xxxvi. 331.

[3] Winkler, *Repert. Pharm.* lxvii. 1, 56.

[4] *Jahresb. Chem.* iv. 519.

[5] *Loc. cit.*; Ittner, *ibid.* xxiv. 395.

[6] *Ann. Chem. Pharm.* lxxxv. 183.

[7] Müller and Limpricht, *ibid.* cxi. 136.

[illegible]

[illegible] distillation.

[illegible] of almonds.[1]

[illegible] perfumery, and [illegible] used with care. [illegible] are used in [illegible]

[illegible] other ways, some of [illegible] benzyl compounds. [illegible] oxidation of cinnamic acid C_6H_5CH [illegible] Müller prepared it in a similar manner from oil of cinnamon, which contains cinnyl aldehyde,[1] and Toel from styrone or cinnyl alcohol, $C_6H_5.CH=CH.CH_2.OH$.[2] Various other allied aromatic compounds yield benzaldehyde on oxidation. Cannizzaro showed that it is the first product of the oxidation of benzyl alcohol (p. 91), while Guckelberger and Keller found it among the products which are formed by the action of potassium permanganate and sulphuric acid on the albuminoids.[3]

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[1] [illegible] 116.
[2] Flückiger and Hanbury, *Pharmacographia*, 2nd ed. 250.
[3] [illegible] *Bull. Soc. Chim.* [2] viii. 152.
Ann. Chem. Pharm. [illegible] 385.
[4] [illegible] *Pharm.* cxxii. 77.

It is readily obtained from benzoic acid by reduction carried on in aqueous solution by means of sodium amalgam,[4] or by heating with stannous oxide.[5] Baeyer obtained it by passing the vapour of benzoic acid or of phthalic acid, $C_6H_4(CO_2H)_2$, over heated zinc-dust[6] and Chiozza by the action of copper hydride on benzoyl chloride.[7] Piria found that it is formed by distilling a mixture of calcium benzoate and formate.[8]

When the vapour of benzene or toluene, mixed with air, is brought into contact with a glowing spiral of platinum or palladium, benzoic acid is formed together with some benzaldehyde, which is formed in larger quantity from xylene (dimethylbenzene) or cymene (methylpropylbenzene.)[9] Toluene, as already mentioned (p. 6), forms a compound with chromium oxychloride, which is decomposed by water with formation of benzaldehyde.

This is also formed when benzyl chloride is boiled with dilute nitric acid or water and lead nitrate,[10] as well as by heating benzidene chloride, $C_6H_5.CHCl_2$, with silver oxide, mercuric oxide,[11] or alcoholic potash,[12] or with water to 140°—160°.[13] When this compound is heated with two molecules of sulphuric acid to 30°, hydrochloric acid is evolved and a syrupy liquid formed, which is decomposed by water into sulphuric acid and benzaldehyde.[14]

On the small scale benzaldehyde is best prepared by gradually heating benzidene chloride to 130° with the necessary amount of anhydrous oxalic acid :

$$C_6H_5.CHCl_2 + C_2H_2O_4 = C_6H_5.CHO + CO + CO_2 + 2HCl.$$

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[1] *Journ. Prakt. Chem.* xviii. 385.

[2] *Ann. Chem. Pharm.* lxx. 5.

[3] *Ibid.* lxiv. 60 ; lxxii. 86.

[4] Kolbe, *ibid.* cxviii. 122.

[5] Dusart, *Compt. Rend.* lv. 448.

[6] *Ann. Chem. Pharm.* cxl. 296.

[7] *Ibid.* lxxxv. 232.

[8] *Ibid.* c. 105.

[9] Coquillon, *Compt. Rend.* lxxvii. 444 ; lxxx. 1089.

[10] Grimaux and Lauth, *Bull. Soc. Chim.* [2] vii. 106.

[11] Gerhardt, *Traité Chim.* iv. 721.

[12] Cahours, *Ann. Chem. Pharm.* Suppl. ii. 253.

[13] Limpricht, *ibid.* cxxxix. 319.

[14] Oppenheim, *Ber. Deutsch. Chem. Ges.* ii. 213.

The residue is distilled under diminished pressure, and the aldehyde purified by a single rectification.[1]

2087 Benzaldehyde is manufactured by boiling 2 parts of benzyl chloride with 3 parts of lead nitrate, or better, copper nitrate, and 10 parts of water for several hours in an apparatus connected with an inverted condenser, the operation being conducted in a current of carbon dioxide; half the liquid is then distilled off, and the oil separated from the water. It is obtained from benzidene chloride by heating it under pressure in an iron vessel with caustic soda. According to Espenschied it is possible to heat without pressure in an apparatus connected with an inverted condenser if milk of lime be used, or if whitening, or some other finely-divided insoluble substance, be added and the whole stirred into an emulsion, which boils at a higher temperature and thus facilitates the decomposition of the chloride. Jacobsen recommends a process in which benzidene chloride is heated with glacial acetic acid and zinc chloride, benzaldehyde and acetyl chloride being formed; the necessary amount of water is then allowed to flow in, and the acetic acid which is formed, recovered.[2]

The benzaldehyde thus obtained, which always contains chlorine compounds, is used in the colour industry. The pure compound may be obtained from it by preparing the double sulphite, which has already been mentioned, and decomposing this with caustic soda solution.

Properties.—Benzaldehyde is a colourless, strongly refractive liquid which has a well known characteristic smell and a burning aromatic taste. It dissolves in more than 300 parts of water;[3] boils at 179°, and has a specific gravity of 1·0636 at 0° and of 1·0504 at 15°. In the pure state it rapidly oxidizes in the air and is also oxidized by boiling with chromic acid solution, manganese dioxide and sulphuric acid, or freshly precipitated ferric oxide.[4] It is, however, only slowly attacked by strong, boiling nitric acid; the red, fuming acid only yields benzoic acid, but when mixed with sulphuric acid gives substitution products.[5] It differs from the aldehydes of the fatty series in not reducing an alkaline copper solution.[6]

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[1] Anschütz, *Liebig's Ann.* ccxxvi. 18.

[2] *Ber. Deutsch. Chem. Ges.* xiii. 2013; xiv. 1425.

[3] Flückiger, *Jahresb. Chem.* 1875, 182.

[4] Gräger, *Ann. Chem. Pharm.* cxi. 124.

[5] Lippmann and Hawliczek, *Ber. Deutsch. Chem. Ges.* ix. 1463.

[6] Tollens, *ibid.* xiv. 1950.

It is converted into benzyl alcohol by treatment with sodium amalgam and water; hydrobenzoin is simultaneously formed, together with the isomeric isohydrobenzoin $C_{14}H_{12}(OH)_2$, which compounds, together with benzoin, $C_6H_5.CH(OH)CO.C_6H_5$, obtained by heating benzaldehyde with alcoholic potassium cyanide solution, will be subsequently described.

Benzaldehyde is not poisonous; when taken internally it appears in the urine as hippuric acid;[1] it is not decomposed when heated to dull redness, but is decomposed, chiefly into benzene and carbon monoxide, when passed through a tube filled with pumice stone and heated to bright redness.[2]

Benzaldehyde readily combines with other carbon compounds with elimination of water and is therefore largely employed, both on the small and large scale, for the synthesis of condensation products, which will be subsequently described. Only a few of the most important reactions will be mentioned here.

(1.) When benzaldehyde is heated with sodium acetate and acetic anhydride, cinnamic acid, $C_6H_5.CH{=}CH.CO_2H$, is formed. The homologues of this acid are prepared in an analogous manner from the other fatty acids.

(2.) Aromatic ketones are easily obtained by the condensation of a fatty ketone with benzaldehyde; thus ordinary acetone yields methylcinnyl ketone, $CH_3.CO.CH{=}CH.C_6H_5$, which is converted by the further action of benzaldehyde into dicinnyl ketone or cinnamone, $CO(CH{=}CH.C_6H_5)_2$.

(3.) When benzaldehyde is heated with aniline and zinc chloride, diamidotriphenylmethane, $C_6H_5.CH(C_6H_4.NH_2)_2$, is obtained; if dimethylaniline be employed, the base, $C_6H_5.CH(C_6H_4.N.(CH_3)_2)_2$, is formed, and this yields on oxidation the colouring matter known as benzaldehyde-green or malachite-green.

(4.) Benzaldehyde combines with the nitroparaffins to form aromatic nitro-olefines, such as phenylnitro-ethylene, $C_6H_5.CH{=}CHNO_2$, etc.

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[1] Frerichs and Wöhler, *Ann. Chem. Pharm.* lxv. 337.

[2] Barreswill and Boudault, *ibid.* lii. 360.

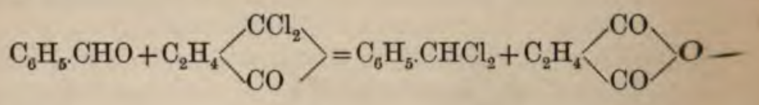
BENZIDENE COMPOUNDS.

2088. Benzaldehyde, like other aldehydes, behaves as the oxide of a dyad radical, which is called benzylene, benzylidene or benzidene. As in all analogous cases, the corresponding alcohol cannot be prepared, but ethers, ethereal salts, and other derivatives are known.

Benzidene diethyl ether, $C_6H_5.CH(OC_2H_5)_2$, was obtained by Wicke by the action of benzidene chloride on sodium othylate. It is a liquid which possesses a pleasant smell resembling that of the geranium, and boils at 222°. Wicke has also prepared various other ethers.[1]

Benzidene dichloride, $C_6H_5.CHCl_2$. Cahours prepared this compound by the action of phosphorus pentachloride on oil of bitter almonds[2] and named it *chlorobenzol*, a name which was subsequently changed into chloride of oil of bitter almonds and finally into benzal chloride (benzaldehyde chloride), which is still employed.

It is also obtained by treating benzaldehyde with carbonyl chloride or succinyl chloride:[3]



$$C_6H_5.CHO + C_2H_4\left\langle\begin{matrix}CCl_2\\CO\end{matrix}\right\rangle = C_6H_5.CHCl_2 + C_2H_4\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle O$$

It is, however, most readily prepared by passing chlorine into boiling toluene until it has gained 75 per cent. in weight and then purifying the product by fractional distillation.[4]

It is a colourless liquid which boils at 206°—207° and has a specific gravity of 1·295 at 16°.[5] In the cold it has only a feeble smell, but when heated it gives off a penetrating vapour which produces a flow of tears. It is manufactured and employed for the preparation of benzaldehyde.

Benzidene dibromide, $C_6H_5.CHBr_2$, is formed by the action of phosphorus pentabromide on benzaldehyde; it is a powerfully refractive liquid, which can only be distilled without decomposition under considerably reduced pressure.[1]

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[1] Wicke, *Ann. Chem. Pharm.* cii. 363.

[2] *Ann. Chim. Phys.* [3] xxiii. 329.

[3] Rembold, *Ann. Chem. Pharm.* cxxxviii. 189.

[4] Beilstein and Kuhlberg, *ibid.* cxlvi. 322.

[5] Hübner and Bente, *Ber. Deutsch. Chem. Ges.* vi. 804.

Benzidene di-iodide, $C_6H_5.CHI_2$. Geuther and Cartmell, by the action of hydriodic acid gas on benzaldehyde, obtained a peculiar compound, which they named *benzaldehyde oxyiodide*, $C_{21}H_{18}I_4O$; it forms colourless, rhombic tablets, which melt at 28° and rapidly become coloured dark in the light. It smells exactly like cress, and can be volatilized with steam, yielding a vapour which attacks the eyes and nose most violently, the pain caused being greater and more enduring than that produced by acrolein. When it is heated with silver nitrate solution, a smell of benzaldehyde is produced.[2]

The constitution of this body, the formula of which can be expressed as $C_6H_5.CHO + 2C_6H_5.CHI_2$, is unknown.

Benzidene diacetate, $C_6H_5.CH(C_2H_3O_2)_2$. Wicke obtained this compound by the action of silver acetate on benzidene chloride;[3] it is also formed when benzaldehyde is heated with acetic anhydride,[4] and crystallizes from ether in small, monoclinic tablets or in twins, which have the swallow-tail form of crystals of gypsum. It melts at 45°—46°,[5] and boils at 220°.[6]

Wicke has also prepared some other ethereal salts of benzidene.

Potassium benzidene sulphite, $C_6H_5.CH(OH)SO_3K$. This compound, which was earlier called the bisulphite of benzaldehyde-potash, was obtained by Bertagnini in crystals by agitating benzaldehyde with a concentrated solution of acid potassium sulphite.[7] It crystallizes from hot, dilute alcohol in long plates, which are slightly soluble in cold alcohol, readily in water, but are almost insoluble in a concentrated solution of acid potassium sulphite. It is decomposed by simply boiling with water, more readily by acids or alkalis, with separation of benzaldehyde, which can thus be obtained pure (p. 134).

Sodium benzidene sulphite, $C_6H_5.CH(OH)SO_3Na + H_2O$, forms small crystals, and behaves like the potassium salt.

Ammonium benzidene sulphite, $C_6H_5.CH(OH)SO_3NH_4 + H_2O$. Bertagnini, on shaking benzaldehyde with a concentrated solution of acid ammonium sulphite, observed an evolution of heat and obtained a clear solution from which no crystals separated out.

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[1] Michaelson and Lippmann, *Ber. Deutsch. Chem. Ges.* Suppl. iv. 113.

[2] *Ann. Chem. Pharm.* cxii. 20.

[3] *Ibid.* cii. 368.

[4] Geuther, *ibid.* cvi. 251; Hübner, *Zeitschr. Chem.* 1867, 277.

[5] Perkin, *ibid.* 1868, 172.

[6] Neuhof, *Ann. Chem. Pharm.* cxlvi. 323.

[7] *Ibid.* lxxxv. 183.

Otto, however, obtained the compound in crystals by mixing alcoholic solutions of sulphur dioxide and hydrobenzamide; a precipitate is formed consisting of microscopic needles which are slightly soluble in alcohol, readily in water, and separate from the latter in transparent crystals containing three molecules of water.[1]

Benzaldehyde does not form an analogous compound with acid aniline sulphite, but a very stable substance of the empirical formula, $2C_7H_6O + 2C_6H_7N + SO_2$, is produced, and crystallizes from water in long, flat needles.[2]

Benzidene sulphide, $C_6H_5.CHS$. Cahours prepared this compound by heating benzidene chloride with an alcoholic solution of potassium hydrosulphide and named it sulphobenzene.[3] It was then further investigated by Fleischer[4] and Böttinger.[5] It crystallizes from hot alcohol in nacreous plates and from ether in transparent, four-sided prisms, melting at 70°—71°. On heating with caustic potash it yields benzyl hydrosulphide, benzyl disulphide and some benzoic acid, and on dry distillation gives stilbene, $C_{14}H_{12}$, tolallyl sulphide, $C_{14}H_{10}S$, and thionessal, $C_{28}H_{20}S$.

Parabenzidene sulphide, $(C_6H_5.CHS)_n$. By the action of ammonium sulphide on an alcoholic solution of benzaldehyde, Laurent obtained a compound of this composition, which he called sulphobenzoyl hydride (*hydrure de sulfobenzoïle*), and described as a powder consisting of microscopic granules, which became soft at 90°—95°, and, after careful fusion, solidified to a transparent mass. It is odourless, but imparts to the hands a very repulsive, adhering alliaceous odour.[6] On dry distillation it yields the same products as benzidene sulphide.

The compound which Klinger obtained by passing sulphuretted hydrogen into a solution of benzaldehyde in absolute alcohol and named *a-benzothio-aldehyde*, is probably identical with this body. It is amorphous, softens at 80°—85°, and is converted by acid chlorides into *β-benzothio-aldehyde*, which is slightly soluble in alcohol, readily in hot glacial acetic acid, and crystallizes in lustrous white needles, melting at 225°—226°.[7]

This compound is most readily obtained by dissolving amorphous benzothio-aldehyde in hot benzene and adding a small quantity of iodine also dissolved in benzene; lustrous needles of the formula $C_6H_5.CHS + C_6H_6$ soon separate out, which lose benzene and become opaque at 125°—130°.[1]

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[1] Neuhof, *Ann. Chem. Pharm.* cxii. 308.

[2] Schiff, *ibid.* cxl. 130; ccx. 128.

[3] *Ann. Chim. Phys.* [3] xxiii. 333; *Ann. Chem. Pharm.* lxx. 40.

[4] *Ibid.* cxl. 234.

[5] *Ber. Deutsch. Chem. Ges.* xii. 1053.

[6] *Ann. Chim. Phys.* [3] i. 292; *Ann. Chem. Pharm.* xxxviii. 320; see also Rochleder, *ibid.* xxxvii. 346.

[7] *Ber. Deutsch. Chem. Ges.* ix. 1893.

α-Benzothio-aldehyde is also formed, together with ammonia, when an alkaline solution of benzothiamide, $C_6H_5.CS.NH_2$, is treated with sodium amalgam.[2]

Both thio-aldehydes, when heated with copper dust, yield stilbene, $C_{14}H_{10}$, as the chief product, and the amorphous compound on fusion with caustic potash yields the same products as benzidene sulphide (Böttinger). Klinger was unable to convert the latter, which he considered to be *γ-benzothio-aldehyde*, into the β-compound by the action of acetyl chloride or iodine; the β-compound is probably a polymeric modification, and is best called parabenzidene sulphide.

2089 *Benzidenoxime*, or *Benzaldoxime*, $C_6H_5.CH.NOH$, is formed when benzaldehyde and sufficient alcohol to form a clear solution are added to an aqueous solution of hydroxylamine hydrochloride containing an excess of sodium carbonate:

$$C_6H_5.CHO + H_2N.OH = C_6H_5.CH{=}N.OH + H_2O.$$

After twenty-four hours the mixture is extracted with ether and the residue, after the evaporation of the ether, rectified.

Benzaldoxime is an oily liquid, which boils above 220° with partial decomposition, and is decomposed by hydrochloric acid into the substances from which it is formed. On treatment with alcoholic caustic soda it gives the compound $C_6H_5.CH.NONa$, which crystallizes from water in small, lustrous plates. By the action of methyl iodide on this, the methyl ether, $C_6H_5.CH,NOCH_3$, is obtained as a light, oily liquid, which has a very pleasant, fruity odour, and boils at 190°—192°; other ethers have been prepared in a similar manner.[3]

Hydrobenzamide, or *Tribenzidenediamine*, $N_2(CH.C_6H_5)_3$. Acetaldehyde combines directly with ammonia to form aldehyde ammonia, $CH_3.CH(OH)NH_2$, but benzaldehyde behaves in a completely different manner; three molecules of the latter lose all their oxygen, which combines with the hydrogen of two molecules of ammonia, the place of this being taken by the benzidene groups.

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[1] *Ber. Deutsch. Chem. Ges.* x. 1877.
[2] Bernthsen, *ibid.* x. 36.
[3] Petraczek, *ibid.* xv. 2783; xvi. 823.

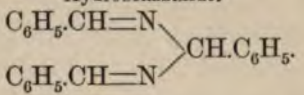
Hydrobenzamide is slowly formed when benzaldehyde is allowed to stand in contact with aqueous ammonia;[1] more rapidly when the two are heated together.[2]

Benzaldehyde absorbs dry ammonia, and if the product of this absorption be allowed to stand in a vacuum, water is lost and hydrobenzamide remains;[3] it is also formed when benzidene-dichloride is allowed to stand for some months with aqueous ammonia.[4]

It is readily soluble in alcohol and ether, and crystallizes in lustrous, rhombic pyramids, melting at 110°; very fine crystals may be obtained by pouring an excess of aqueous ammonia on to a mixture of equal volumes of benzaldehyde and ether, and allowing the whole to stand.[5] It is tasteless, but its alcoholic solution has, according to Laurent, a faint taste of burnt almonds. On boiling with alcohol it slowly decomposes into ammonia and benzaldehyde; acids rapidly produce this decomposition. On oxidation with aqueous chromic acid, a large quantity of benzoic acid is formed (Fownes).

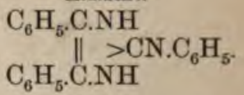
When it is boiled with caustic potash or heated to 120°—130°, it is converted into the isomeric amarine, which will be subsequently described; the relation between the two compounds is shown by the following formulæ:

Hydrobenzamide.



$$\begin{matrix} C_6H_5.CH{=}N \\ C_6H_5.CH{=}N \end{matrix}\!\!>\!CH.C_6H_5.$$

Amarine.



$$\begin{matrix} C_6H_5.C.NH \\ \| \\ C_6H_5.C.NH \end{matrix}\!\!>\!CN.C_6H_5.$$

Thiobenzaldine, $(C_6H_5.CH)_3S_2NH$. Laurent obtained this compound, the analogue of thialdine (Pt. II. p. 75), by allowing a mixture of crude oil of bitter almonds, ammonium sulphide and ether, to stand for several weeks. It crystallizes in nacreous plates or monoclinic prisms which melt at 125°, and impart an unpleasant smell to the skin. When it is boiled with alcohol, sulphuretted hydrogen is given off, while alcoholic potash decomposes it with evolution of ammonia.[6]

Benzidene-aniline, $C_6H_5.CH{=}N.C_6H_5$. Gerhardt and Laurent obtained this compound by heating benzaldehyde with aniline, and named it benzoylanilide.[1] The same compound is formed, as shown by Schiff, when benzaldehyde is heated with thiocarbanilide:[2]

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[1] Laurent (1836), *Ann. Chim. Phys.* lxii. 23; lxvi. 18; *Ann. Chem. Pharm.* xxi. 130.

[2] Rochleder, *ibid.* xli. 89.

[3] Herzfeld, *Ber. Deutsch. Chem. Ges.* x. 1271.

[4] Engelhardt, *Ann. Chem. Pharm.* cx. 77.

[5] Eckmann, *ibid.* cxii. 175.

[6] *Ann. Chem. Pharm.* xxxviii. [illegible]3.

$$3CS(NHC_6H_5)_2 + 6C_6H_5.CHO =$$
$$6C_6H_5.CH{=}N.C_6H_5 + CS_2 + 2CO_2 + H_2S + 2H_2O.$$

It is very soluble in alcohol and ether, separating from the latter in warty crystals, and crystallizing from carbon disulphide in yellow needles, which melt at 42°,[3] and are volatile with steam. It does not combine with acids, and is partially decomposed on heating into benzaldehyde and aniline.

2090 *Benzidene-aniline cyanhydrate*, $C_6H_5.CH{=}N.C_6H_5.CNH$. Cech obtained this compound by the action of potassium cyanide on an alcoholic solution of benzaldehyde and aniline or aniline hydrochloride; it is also formed when hydrocyanic acid is passed into fused benzidene-aniline, and is decomposed into its components by heat. It crystallizes from carbon disulphide in silky needles, which melt at 82°, sublime readily, and are volatile with steam.

Benzidenephenylhydrazine, $C_6H_5.CH{=}N.NH.C_6H_5$, is formed by a violent reaction when benzaldehyde and phenylhydrazine are brought together. It crystallizes from dilute alcohol in monoclinic prisms, which melt at 152·5° and can be volatilized without decomposition.

Benzidenediphenylhydrazine, $C_6H_5.CH{=}NC.(C_6H_5)_2$, forms small yellow crystals, melting at 122°.[4]

Phenylbenzaldehydine, or *Benzidene-orthodiamidobenzene*, $(C_6H_5.CH{=}N)_2C_6H_4$, is formed when a dilute aqueous solution of orthodiamidobenzene hydrochloride is shaken up with benzaldehyde, the hydrochloride thus obtained being purified by re-crystallization, and the base precipitated with caustic potash.

Phenylbenzaldehydine is insoluble in water and crystallizes from alcohol in six-sided prisms, melting at 133°—134°.

Phenylbenzaldehydine hydrochloride, $C_{20}H_{16}N_2.HCl$, crystallizes in colourless prisms which are only slightly soluble in water, and lose hydrochloric acid when their solution is boiled.

When the base is heated with ethyl iodide to 100°—120°, the compound $C_{20}H_{16}N_2.C_2H_5I$ is formed; it crystallizes from hot water in colourless, thick prisms, melting at 211°—213°.[5]

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[1] *Jahresb. Chem.* 1850, 488.

[2] *Ann. Chem. Pharm.* cxlviii. 336.

[3] Cech, *Ber. Deutsch Chem. Ges.* xi. 246.

[4] E. Fischer, *Ann. Chem. Pharm.* cxc. 134, 179.

[5] Engelbrecht and Ladenburg, *Ber. Deutsch. Chem. Ges.* xi. 1653.

Benzideneparadiamidobenzene, $(C_6H_5.CH{=}N)_2C_6H_4$, is formed by the action of paradiamidobenzene on benzaldehyde; it crystallizes from alcohol in plates which have a silver lustre, and melt at 140°; it is decomposed by acids into its components, since only the ortho-diamines form stable basic aldehydines[1] (Part III. p. 62).

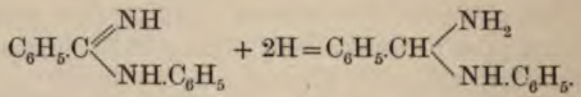
Benzidenedimethylparadiamidobenzene, $C_6H_5.CH{=}N.C_6H_4.N(CH_3)_2$, is readily formed by heating benzaldehyde with dimethylparadiamidobenzene, and crystallizes from hot alcohol in lustrous plates or needles, melting at 93°. It is a feeble, di-acid base.[2]

Dibenzidene-orthodiamidotoluene, or *Tolubenzaldehydine*, $(C_6H_5.CH{=}N)_2C_6H_3.CH_3$, has been obtained by Ladenburg from orthodiamidotoluene; it crystallizes in lustrous, monoclinic prisms, melting at 195·5°; on oxidation with potassium permanganate, it yields *dibenzidenediamidobenzoic acid*, $(C_6H_5.CH{=}N)_2.C_6H_3CO_2H$. The hydrochloride, $C_{21}H_{18}N_2.ClH$, crystallizes from hot dilute hydrochloric acid in long needles.

When it is heated with ethyl iodide, it is converted into the iodide, $C_{21}H_{18}N_2.C_2H_5I$, which crystallizes in thick prisms, and, on treatment with silver oxide, yields the corresponding hydroxide, which remains behind after evaporation of the solution as a strongly alkaline, oily liquid.[3]

Dibenzidenemetadiamidotoluene crystallizes from a mixture of ether and alcohol in small lustrous tablets, melting at 122°—128°. It does not combine with acids, but when heated to 140°—150° for a considerable time, it is converted into a base, which Schiff considers to be amarine.[4]

Benzidenephenyldiamine, $C_6H_5.CH(NH_2)NH(C_6H_5)$. When benzonitril, $C_6H_5.CN$, is heated with aniline hydrochloride to 220°—240°, phenylbenzenylamidine[5] is formed, and this is converted into the diamine by the action of zinc and dilute acetic acid:



$$C_6H_5.C\begin{matrix}\diagup NH\\ \diagdown NH.C_6H_5\end{matrix} + 2H = C_6H_5.CH\begin{matrix}\diagup NH_2\\ \diagdown NH.C_6H_5\end{matrix}.$$

It is very soluble in all solvents, with the exception of water and separates from dilute alcohol in indistinct crystals, melting at

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[1] Ladenburg, *Ber. Deutsch. Chem. Ges.* xi. 599.
[2] Calm, *ibid.* xvii. 2938.
[3] *Ibid.* x. 1126; xi. 591, 1648.
[4] *Ann. Chem. Pharm.* cxl. 98.
[5] Bernthsen, *Liebig's Ann.* clxxxiv. 348.

114·5°—115°. At a higher temperature it distils without decomposition, and on heating with chloroform and alcoholic potash yields the smell of the carbamines.

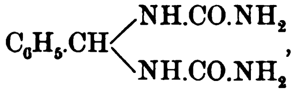
Benzidenephenylamine hydrochloride, $C_{13}H_{14}N_2.ClH$, crystallizes from water in thick prisms, melting at 223°—224·5°.[1]

Benzidene-acetamide, $C_6H_5.CH(NH.C_2H_3O)_2$, is formed by heating benzaldehyde with acetamide, and crystallizes from hot water in fine silky needles.[2]

Benzidene urethane, $C_6H_5.CH(NH.CO.OC_2H_5)_2$, is formed when hydrochloric acid is added to a mixture of benzaldehyde and ethyl carbamate. It separates from alcohol as a silky crystalline mass, which melts at 171°, and can be sublimed.[3]

Benzidene ureïdes are formed by heating benzaldehyde with urea, and are split up again into these substances by boiling with water.[4]

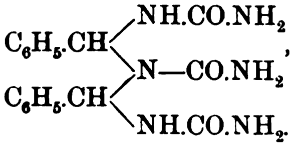
Benzidenedi-ureïde,



$$C_6H_5.CH\left\langle\begin{array}{l}NH.CO.NH_2\\NH.CO.NH_2\end{array}\right.$$

, fine needles.

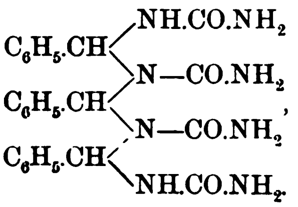
Benzidenetri-ureïde,



$$\begin{array}{l}C_6H_5.CH\left\langle\begin{array}{l}NH.CO.NH_2\\ \end{array}\right.\\ \qquad\qquad\rangle N—CO.NH_2\\ C_6H_5.CH\left\langle\begin{array}{l}\\ NH.CO.NH_2.\end{array}\right.\end{array}$$

, white powder.

Benzidenetetra-ureïde,



$$\begin{array}{l}C_6H_5.CH\left\langle\begin{array}{l}NH.CO.NH_2\\ \end{array}\right.\\ \qquad\qquad\rangle N—CO.NH_2\\ C_6H_5.CH\langle\\ \qquad\qquad\rangle N—CO.NH_2\\ C_6H_5.CH\left\langle\begin{array}{l}\\ NH.CO.NH_2.\end{array}\right.\end{array}$$

, white powder.

SUBSTITUTION PRODUCTS OF BENZIDENE COMPOUNDS.

2091 *Orthochlorobenzaldehyde*, $C_6H_4Cl.CHO$. By the action of phosphorus pentachloride on salicylaldehyde, $C_6H_4(OH)CHO$, *orthochlorobenzidene chloride*, $C_6H_4Cl.CHCl_2$, is obtained as an oily liquid, which boils at 227°—230°, and possesses a penetrating smell and a sharp burning taste. When this compound is heated with water to 170°, the aldehyde is formed; it is a liquid which boils at 210°, has a sharp smell and taste, and readily oxidizes in the air to orthochlorobenzoic acid. It combines with acid sodium sulphite.[1]

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[1] Bernthsen and Scymanski, *Ber. Deutsch. Chem. Ges.* xiii. 917.

[2] Roth, *Ann. Chem. Pharm.* cliv. 72.

[3] Bischoff, *Ber. Deutsch. Chem. Ges.* vii. 634, 1082.

[4] Schiff, *Ann. Chem. Pharm.* cxl. 115 ; cxlviii. 330 ; cli. 802.

Metachlorobenzaldehyde is formed when benzaldehyde is chlorinated in presence of a dehydrating agent, such as sulphuric acid, zinc chloride, aluminium chloride, etc., and is a liquid boiling at 210°—213°.[2]

It may also be obtained by heating a hydrochloric acid solution of metamidobenzaldehyde and cuprous chloride to the boiling-point and then gradually adding a solution of sodium nitrite.[3]

Parachlorobenzaldehyde is obtained by boiling parachlorobenzyl bromide with water and lead nitrate in an atmosphere of carbon dioxide. It crystallizes in white tablets, melting at 47·5°, which are slightly soluble in cold, more readily in hot water, and readily in alcohol; it smells like benzaldehyde, readily oxidizes in the air and unites with acid sodium sulphite to form a compound which is only slightly soluble.[4]

The product of the action of chlorine on benzidene chloride in presence of iodine is a mixture of ortho- and para-chlorobenzidene chlorides, which boils at 230°—237°,[5] and was formerly thought to be the pure para-compound.[6] When it is heated with anhydrous oxalic acid, boiled with lead nitrate, or heated to 170° with water, a mixture of the aldehydes is obtained, boiling at 210°—214°; in the cold it smells like benzaldehyde, but when heated has a very sharp, penetrating odour and causes a flow of tears. The same mixture is formed, together with ethyl iodide, when benzyl ethyl ether is treated with chlorine in presence of iodine:[7]

$$C_6H_5.CH_2.O.C_2H_5 + ICl_3 = C_6H_4Cl.CHO + C_2H_5I + 2HCl.$$

Dichlorobenzaldehyde, $C_6H_3Cl_2.CHO(Cl : Cl = 3 : 4)$. Beilstein and Kuhlberg, by the action of chlorine on boiling dichlorotoluene, obtained a *dichlorobenzidene chloride*, $C_6H_3Cl_2.CHCl_2$,[1] which boils at 257°, and is converted into the aldehyde by heating with water to 200°. It is soluble in boiling water, more readily in alcohol, and crystallizes in fine needles, which melt at 68°, volatilize in steam, and combine with acid sodium sulphite.[2] A compound, which is probably identical with this, is obtained by the further chlorination of metachlorobenzaldehyde in presence of a dehydrating agent, and is described as a liquid, boiling at 240°—243°.[3]

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[1] Henry, *Ber. Deutsch. Chem. Ges.* ii. 135.
[2] Müller, *ibid.* xviii. Ref. viii. 680.
[3] *Ibid.* xviii. Ref. 595.
[4] Jackson and White, *ibid.* xi. 1042.
[5] Anschütz, *Ann. Chem. Pharm.* ccxxvi. 19.
[6] Beilstein and Kuhlberg, *ibid.* cxlvi. 327.
[7] Sintenis, *Ber. Deutsch. Chem. Ges.* iv. 699.

α-Trichlorobenzaldehyde, $C_6H_2Cl_3.CHO$. The further chlorination of α-trichlorotoluene yields *α-trichlorobenzidene chloride*, $C_6H_2Cl_3.CHCl_2$, which boils at 280°—281°, and solidifies below 0° in fine needles.[4] The aldehyde obtained by heating it with water to 260° is insoluble in water, crystallizes in very fine needles, which melt at 112°—113°, and is volatile with steam.[5]

β-Trichlorobenzaldehyde. The *β-trichlorobenzidene chloride* obtained from β-trichlorotoluene, melts at 84°, boils at 280°, and yields the β-trichlorobenzaldehyde which melts at 90° (Seelig).

Tetrachlorobenzidene chloride, $C_6HCl_4.CHCl_2$, has been prepared from tetrachlorotoluene; it is a liquid, which boils at 305°—306°, and is decomposed by water at 250°. The aldehyde thus formed has not been further investigated.[6]

Pentachlorobenzidene chloride, $C_6Cl_5.CHCl_2$, is formed by the continued action of chlorine on benzidene chloride in presence of iodine and finally of antimony chloride. It crystallizes from alcohol in long flat plates, melts at 109°, boils at 334°, and is not attacked by water even at 300°.[7]

Orthobromobenzaldehyde, $C_6H_4Br.CHO$, has been prepared by boiling orthobromobenzyl bromide with water and lead nitrate; it is a heavy, oily liquid, which oxidizes very rapidly in the air.[8]

Metabromobenzaldehyde, $C_6H_4Br.CHO$, is a liquid which does not solidify in a freezing mixture (Jackson and White), boils at 233°—236°, and may be prepared by the bromination of benzaldehyde in presence of a dehydrating agent (Müller).

Parabromobenzaldehyde, $C_6H_4Br.CHO$, crystallizes in long white needles, melting at 57°.

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[1] *Ann. Chem. Pharm.* cl. 291.

[2] *Ibid.* clii. 228.

[3] *Ber. Deutsch. Chem. Ges.* Ref. xviii. 25.

[4] *Ann. Chem. Pharm.* cl. 299; Seelig, *Ber. Deutsch. Chem. Ges.* xviii. 420.

[5] *Ibid.*; *Ann. Chem. Pharm.* clii. 238.

[6] *Ibid.* cl. 303.

[7] *Ibid.* cl. 306.

[8] Jackson and White, *Amer. Chem. Journ.* iii. 32.

Para-iodobenzaldehyde, $C_6H_4I.CHO$, also forms needles, melting at 73° (Jackson and White).

2092 *Orthonitrobenzaldehyde*, $C_6H_4(NO_2)CHO$, is formed in small quantity, together with the meta-compound, by the action of a mixture of nitric and sulphuric acids on benzaldehyde.[1] It may, however, be more readily prepared from orthonitrocinnamic acid, $C_6H_4(NO_2)CH{=}CH.CO_2H$. When the ethyl ether of this acid is dissolved in concentrated nitric acid and treated with sodium nitrite, the temperature of the mixture not being allowed to rise more than a few degrees, a compound is formed which contains a nitric acid residue in the side chain. The mixture is poured, after having stood for some hours, into water, and the oil which separates out distilled in steam, sodium carbonate being added from time to time; the distillate consists of water and pure orthonitrobenzaldehyde.[2] It can be still more conveniently prepared by oxidizing orthonitrocinnamic acid with potassium permanganate in alkaline solution (Friedländer and Henriques). The solution must be cooled with ice and shaken up with benzene at short intervals in order to remove the aldehyde from the further action of the oxidizing agent. The benzene solution is then evaporated, the aldehyde remaining behind.[3]

It is readily soluble in alcohol, slightly in water, and crystallizes in long, light yellow needles, melting at 46°, which smell like benzaldehyde in the cold, but give off a penetrating vapour when heated.

It forms a readily soluble compound with acid sodium sulphite, which crystallizes in small, lustrous plates; concentrated caustic soda solution decomposes it completely into orthonitrobenzyl alcohol and orthonitrobenzoic acid. When a little water and caustic soda are added to its solution in acetone, indigotin, $C_{16}H_{10}N_2O_2$, the colouring matter of indigo, separates out after a short time.[4]

Orthonitrobenzaldoxime, $C_6H_4(NO_2)CH.NOH$. Gabriel and Meyer, by the action of hydrochloric acid and amyl nitrite on amidorthonitrophenylacetic acid, obtained a diazo-compound:

$$NH_2.C_6H_3(NO_2)CH_2.CO_2H + 2NO_2H + HCl =$$
$$ClN = NC_6H_3(NO_2)CH_2NO + CO_2 + 3H_2O.$$

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[1] Rudolph, *Ber. Deutsch. Chem. Ges.* xiii. 310.
[2] Friedländer and Henriques, *ibid.* xiv. 2801.
[3] Einhorn, *ibid.* xvii. 119.
[4] Baeyer and Drewsen, *ibid.* xv. 2857.

On heating with alcohol, this is converted into *nitrosomethylnitrobenzene*, $C_6H_4(NO_2)CH_2NO$, this being decomposed by oxidation with formation of nitrogen monoxide and orthonitrobenzaldehyde, which was first prepared pure by this method.[1]

This substance was subsequently recognised as orthonitrobenzaldoxime and prepared from the aldehyde and hydroxylamine.[2] It crystallizes from hot water in hair-like needles, which melt at 95°, have a sweet taste, and form a yellow solution in alkalis. Its methyl ether, $C_6H_4(NO_2)CH.NOCH_3$, is formed by heating it to 100° with caustic potash, methyl alcohol and methyl iodide; it is only slightly soluble in water, readily in alcohol, and crystallizes in silky needles, melting at 58°.

Metanitrobenzaldehyde, $C_6H_4(NO_2)CHO$, was first obtained by Bertagnini by the action of a mixture of nitric and sulphuric acids on benzaldehyde.[3] In order to prepare it, 1 part of the latter is dissolved in a mixture of 5 volumes of fuming nitric acid with 10 volumes of sulphuric acid, the temperature being kept below 15°. The nitro-compound is precipitated by water, washed and re-crystallized from dilute alcohol.[4] It forms lustrous white needles, melting at 58°,[5] smells like benzaldehyde when cold, but gives off a penetrating vapour when heated, and combines with the acid sulphites of the alkalis (Bertagnini), as well as with acid aniline sulphite[6] to form crystalline compounds.

Metanitrobenzidene chloride, $C_6H_4(NO_2)CHCl_2$, is obtained by the action of phosphorus pentachloride on the aldehyde; it crystallizes from alcohol in needles or small thin plates, melting at 65°.[7]

Metanitrobenzidene bromide, $C_6H_4(NO_2)CHBr_2$, is formed by heating the aldehyde with bromine to 140°, and crystallizes in microscopic tablets, melting at 101°—102°.[8]

Metanitrobenzaldoxime, $C_6H_4(NO_2)CH.NOH$, was first obtained from metanitro-amidophenylacetic acid and was called *nitrosomethylmetanitrobenzene*.[9]

It is readily formed by the combination of hydroxylamine with metanitrobenzaldehyde,[1] and crystallizes from water in long, flat needles, melting at 118°—119°. Its methyl ether also forms flat needles and melts at 63°—63·5°.

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[1] *Ber. Deutsch. Chem. Ges.* xiv. 832, 2332.

[2] Gabriel, *ibid.* xv. 3057.

[3] *Ann. Chem. Pharm.* lxxix. 260.

[4] Widmann, *Ber. Deutsch. Chem. Ges.* xiii. 678; see also Friedländer and Henriques, *ibid.* xiv. 2801.

[5] Lippmann and Hawliczek, *ibid.* ix. 1463.

[6] Schiff, *Ann. Chem. Pharm.* cxcv. 301.

[7] Widmann, *Ber. Deutsch. Chem. Ges.* xiii. 676.

[8] Wachendorff, *Ann. Chem. Pharm.* clxxxv. 266.

[9] Gabriel, *Ber. Deutsch. Chem. Ges.* xv. 834.

Trinitrohydrobenzamide, $N_2(CH.C_6H_4.NO_2)_3$, is formed by the action of ammonia on metanitrobenzaldehyde; it is insoluble in water and ether, and only slightly soluble in boiling alcohol, from which it separates out in flocks consisting of very thin needles. When it is heated to 125° or boiled with dilute caustic potash solution, it is converted into the isomeric *trinitro-amarine*, which forms warty crystals and has a feeble alkaline reaction. Its salts are difficultly soluble and have a very bitter taste (Bertagnini).

Paranitrobenzaldehyde, $C_6H_4(NO_2)CHO$, is prepared by boiling 10 parts of paranitrobenzyl chloride with 60 parts of water, 14 parts of lead nitrate, and 10 parts of nitric acid of sp. gr. 1·3, for several hours. If the solution be more dilute, nitrobenzyl alcohol is formed instead of the aldehyde. The product is shaken out with ether and the aldehyde separated by means of acid sodium sulphite.[2]

Paranitrobenzaldehyde may also be readily obtained by the oxidation of paranitrocinnamic acid.[3] It crystallizes from hot water in thin prisms, often an inch in length, which melt at 106°, have a characteristic smell, and do not volatilize readily in steam. Its compound with acid sodium sulphite is readily soluble in water and crystallizes in small iridescent plates. It is not attacked to an appreciable extent by boiling nitric acid, which must not, however, be too concentrated, but is quantitatively converted into parahydroxybenzoic acid by chromic acid.[4]

When it is heated with aniline hydrochloride and zinc chloride, paranitrodiamidotriphenylmethane, $CH(C_6H_4.NH_2)_2C_6H_4.NO_2$, is formed, which on reduction yields paraleucaniline, $CH(C_6H_4.NH_2)_3$. It is oxidized by mercuric oxide to pararosaniline, $C(OH)(C_6H_4.NH_2)_3$ (Fischer and Greiff).

Paranitrobenzidene chloride, $C_6H_4(NO_2)CHCl_2$, is formed by the action of phosphorus pentachloride on paranitrobenzaldehyde; it crystallizes from alcohol in short, well-formed prisms, melting at 46°.[5]

Paranitrobenzidene bromide, $C_6H_4(NO_2)CHBr_2$, is formed by heating paranitrotoluene with bromine to 140°, and crystallizes from alcohol in needles or small rectangular plates, melting at 82°—82·5°.[1]

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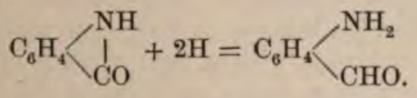
[1] Gabriel, *Ber. Deutsch. Chem. Ges.* xv. 3061.
[2] O. Fischer and Greiff, *ibid.* xiii. 669.
[3] Baeyer, *ibid.* xiv. 2317 ; Friedländer, *ibid.* xiv. 2577 ; Basler, *ibid.* xvi. 2714.
[4] O. Fischer, *ibid.* xiv. 2525.
[5] Zimmermann and Müller, *ibid.* xviii. 996.

Both compounds are converted into pararosaniline when heated with aniline.[2]

Paranitrobenzaldoxime, $C_6H_4(NO_2)CH{=}N.OH$, crystallizes from hot water in long needles, melting at 128·5°.[3]

2093 *Orthamidobenzaldehyde*, $C_6H_4(NH_2)CHO$, was first obtained by Gabriel in small quantities by oxidizing orthamidobenzaldoxime with an acid solution of ferric chloride.[4] Friedländer and Henriques found that orthonitrobenzaldehyde is converted by the action of tin and acetic acid into anthranil,[5] C_7H_5NO, a compound which stands to anthranilic acid or orthamidobenzoic acid in the same relation as lactimide to α-amidopropionic acid (Part II. p. 142). This is converted into orthamidobenzaldehyde by heating with ferrous sulphate and ammonia: [6]



$$C_6H_4\left\langle\begin{matrix} NH \\ | \\ CO \end{matrix}\right. + 2H = C_6H_4\left\langle\begin{matrix} NH_2 \\ \\ CHO. \end{matrix}\right.$$

The latter can also be obtained directly in the same way from orthonitrobenzaldehyde.[7] It is very soluble in alcohol, less readily in water, forming a yellow solution, and crystallizes in lustrous plates, which are volatile with steam, their vapour possessing a penetrating smell resembling that of an indigo vat. It melts at 39°—40°, and solidifies on cooling in a crystalline mass; at a higher temperature a portion distils without decomposition, while the remainder is converted into a dark yellow, resinous mass. It can be heated with caustic soda solution or ammonia without undergoing any change; dilute mineral acids, however, readily convert it into an amorphous condensation product. When it is heated with acetic anhydride, *acetylorthamidobenzaldehyde*, $C_6H_4(NH.C_2H_3O)CHO$, is formed; it crystallizes from hot water in long white needles, melting at 70°—71°.

Orthamidobenzaldoxime, $C_6H_4(NH_2)CH{=}N.OH$, is formed by the reduction of the corresponding nitro-compound with ammonium sulphide, and crystallizes from hot water in long, flat, lustrous needles, melting at 132°—133°.[1]

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[1] Wachendorff, *Ann. Chem. Pharm.* clxxxv. 268.

[2] Zimmermann and Müller, *Ber. Deutsch. Chem. Ges.* xvii. 2936.

[3] Gabriel and Herzberg, *ibid.* xvi. 2000.

[4] *Ber. Deutsch. Chem. Ges.* xv. 2004.

[5] *Ibid.* xv. 2105.

[6] Friedländer, *ibid.* xv. 2572.

[7] Friedländer and Göhring, *ibid.* xvii. 456.

Metamidobenzaldehyde, $C_6H_4(NH_2)CHO$, is obtained by reducing metanitrobenzaldehyde with ammonia and ferrous sulphate, and distilling the product with steam; it is a yellow, oily liquid, which solidifies at low temperatures and yields amorphous condensation products with even greater readiness than the ortho-compound (Friedländer and Göhring).

Metamidobenzaldoxime, $C_6H_4(NH_2)CH{=}N.OH$, is formed when a solution of metanitrobenzaldoxime in caustic soda is added to a hot solution of ferrous sulphate saturated with ammonia, the blue-black ferrous hydroxide being converted into brown ferric hydroxide. The filtrate is rendered faintly acid with hydrochloric acid, treated with ammonia and then extracted with ether; the residue left on evaporation of the ethereal extract consists of metamidobenzaldoxime, which crystallizes from hot benzene in fine, snow-white needles, melting at 88°. Oxidation with an acid solution of ferric chloride yields an amorphous, yellow oxidation product of metamidobenzaldehyde.[2]

Paramidobenzaldehyde, $C_6H_4(NH_2)CHO$, has been obtained as a decomposition product of its aldoxime; it crystallizes from water in small, indented plates, which melt at 69·5°—71·5°, but soon change into a modification insoluble in water and melting at a higher temperature. When heated with acetic anhydride and sodium acetate, it is converted into *acetylparamidobenzaldehyde*, $C_6H_4(NH.C_2H_3O)CHO$, which crystallizes from hot water in long, lustrous needles, melting at 155°.

Paramidobenzaldoxime, $C_6H_4(NH_2)CH{=}N.OH$, is formed by the action of ammonium sulphide on paranitrobenzaldoxime, and crystallizes from hot water in yellow tablets, melting at 124°. It dissolves in an excess of hydrochloric acid, forming a solution which soon deposits dark red needles with a blue reflection, while hydroxylamine remains in solution. Caustic soda decomposes the red compound, paramidobenzaldehyde or its condensation products being set free.[3]

Dimethylparamidobenzaldehyde, $C_6H_4.N(CH_3)_2CHO$. When zinc chloride is allowed to act on a mixture of chloral hydrate and dimethylaniline, dimethylamidophenylhydroxytrichlorethane is formed, and is decomposed by caustic potash with formation of dimethylparamidobenzaldehyde and chloroform or decomposition products of these:

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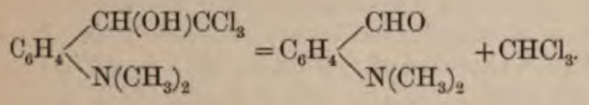
[1] Gabriel and Mayer, *Ber. Deutsch. Chem. Ges.* xiv. 2338.
[2] Gabriel, *ibid.* xvi. 1997.
[3] Gabriel and Herzberg, *ibid.* xvi. 2000.



$$C_6H_4\begin{cases}CH(OH)CCl_3\\N(CH_3)_2\end{cases} = C_6H_4\begin{cases}CHO\\N(CH_3)_2\end{cases} + CHCl_3.$$

The new compound crystallizes in small plates, which melt at 73°, readily dissolve in alcohol and hot water, and are volatile with steam.[1]

BENZOIC ACID, $C_6H_5.COOH$.

2094 The products formed by the dry distillation of gum benzoin[2] are mentioned in writings which date back as far as the sixteenth century. Hieronymus Rosello, who, under the name of Alexius Pedemontanus, published a work, *De Secretis*, in the year 1557, mentions in it the butter of benzoin, and Libavius in his *Alchymia*, written in 1595, says that when *laser*[3] *vel benzoin* is distilled, water comes over first, followed by a thick oil, "*ultima exit instar mannae, gummi.*" Blaise de Vigenère, whose *Traité de feu et du sel*, appeared after his death in 1608, says that with a strong fire "*infinies petites aiguilles et filaments*" appear, which must be soon removed because they would otherwise melt like marrow (*moëlle*). About the same period, Turquet de Mayerne in his *Pharmacopoea* teaches how to obtain flowers of benzoin from the residue by subliming it in an earthen vessel to which a cap of paper has been adapted, or by heating it mixed with sand in a retort, and since that time *flores benzoës* have been an ordinary pharmaceutical preparation. A solution of the resin in alcohol was also in use; mixed with lead acetate it was employed as a choice cosmetic under the names of *magisterium benzoës* or *lac virginis.* Ehrenfried Hagendorn, a physician of Görlitz, in 1671 found in this a salt which was identical with flowers of benzoin, both in smell and taste. Lemery in 1675 also remarked on the acid nature of this substance, saying, "*les fleurs de benjoin ont une acidité fort agréable*," a fact which was further proved by the researches of Scheele, who showed, in 1775, that the flowers of benzoin could be more economically obtained by digesting the resin with slaked lime and water for some hours, boiling and adding hydrochloric acid to the filtrate; finally, Lichtenstein in 1782 conclusively proved that they are an acid.

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[1] Roessneck, *Ber. Deutsch. Chem. Ges.* xviii. 1516; xix. 365.

[2] This resin is obtained by means of incisions in the bark of *Styrax Benzoin*, a tree indigenous to Java and Sumatra. It is sent into the European market from the latter island, and this was formerly the only source from which it could be obtained. A highly valued variety is now sent from Siam, but nothing further is known as to its origin. It was formerly counted as one of the costly spices. It is first mentioned by Ibn Batuta, who travelled in the East about the years 1325—1349, and describes it under the name of Lubán Jáwí (incense of Java). The latter word was then the name of Sumatra, and the Arabs designated by it the whole archipelago, as well as the products obtained from it. The Arabic name gradually became corrupted into banjawi, benjui, benzui, benzoë, benzoïn, and in English also benjamin or gum benjamin, which is now the name in general commercial use (Flückiger and Hanbury, *Pharmacographia*, 2nd ed. p. 403).

[3] Laser is the name of a Persian and Indian product on which a tax was imposed at the Roman customs-house in Alexandria during the second century of our era. Some suppose that it was asa foetida, while benzoë was also called asa dulcis.

The correct composition of benzoic acid was determined in 1832 by Liebig and Wöhler,[1] who showed that it is a compound of the radical benzoyl, C_7H_6O (p. 89). Mitscherlich, on the other hand, showed in 1834 that it is decomposed into carbon dioxide and benzol on heating with milk of lime, and looked upon it as a carbonic acid derivative of benzol; Liebig opposed this view, as he considered the benzol to be merely a product of the destruction of the benzoic acid; the latter compound can, however, as was shown somewhat later, be readily prepared synthetically from carbon dioxide and benzol, and we can therefore look upon it as carbonic acid, $CO(OH)_2$, in which one hydroxyl has been replaced by phenyl, or as a compound of phenyl with carboxyl. The latter supposition corresponds to that of Berzelius, according to which, benzoic acid is oxalic acid copulated with phenyl, oxalic acid being dicarboxyl.

Many varieties of benzoin contain cinnamic acid[2] in addition to benzoic acid and frequently only the former.[3] Both these acids occur, either free or in the form of ethereal salts, together with other aromatic compounds, in Tolu balsam (p. 1), Peru balsam (concerning which Lehmann had already stated in his *Dissertation de balsamo peruviano* (1709), that on decomposition it yields flowers resembling flowers of benzoin), Mecca balsam (*Balsamodendron Opobalsamum et gileadensis*), myrrh (*B. Myrrha*), liquid styrax, acaroïd resin (*Xanthorrheo hastilis*), dragon's blood and other resins. Benzoic acid has also been found in the perfume known as *hilan-hilan* or *ilang-ilang*, which is prepared from the flowers of *Unona odoratissima*,[1] as well as in plums (*Prunus domestica chlorocarpa*)[2] and the cranberry.[3] It also occurs in vanilla, the fruit of the clove-tree, the seeds of the spindle-tree (*Euonymus europaeus*) and the root of the sweet flag (*Acorus calamus*), &c. The coumarin which occurs in *Holcus odoratus*, *Anthoxanthum odoratum* (sweet-scented vernal grass), and woodruff was at one time mistaken for benzoic acid.

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[1] *Ann. Chem. Pharm.* iii. 249.
[2] Kolbe and Lautemann, *ibid.* cxix. 136; Flückiger, *Pharmacographia.*
[3] Aschoff, *Jahresb.* 1861, 400.

In the year 1776, Rouelle stated that the urine of the cow and the camel contains a salt similar to flowers of benzoin, and Scheele, in 1785, obtained a substance, the properties of which agreed with those of benzoic acid, by extracting with alcohol the solid residue left on the evaporation of urine and treating the "soapy extract" with nitric acid. Fourcroy and Vauquelin found, in 1797, that the urine of graminivora contains benzoic acid, but Liebig, in 1829, showed that this substance is a new nitrogenous acid, which he named hippuric acid, and which splits up when the urine is allowed to stand, yielding benzoic acid. According to some observers, however, benzoic acid frequently occurs along with hippuric acid in the urine, and it has also been found in a gland in the beaver,[4] and in the kidneys of the ox.[5] It is probable that in all these cases the acid is formed by the decomposition of hippuric acid.

It has also been observed as a decomposition product of various alkaloids, such as atropine, cotoïne, &c., and is formed in small quantity by the oxidation of albuminoids. It may be obtained in large quantities by the oxidation of those aromatic compounds which possess a side chain containing carbon (Part III. p. 12). It also occurs in coal-tar.[6]

The various synthetical methods by which it has been produced have already been given (Part III. p. 30).

2095 It was formerly prepared exclusively from gum benzoin, and the acid used in medicine is still obtained from it by sublimation; it always contains a small amount of an ethereal oil, which gives it its peculiar smell.[1] In order to obtain it in this way, the coarsely powdered resin is heated to about 170° in a flat iron vessel; this is covered with filter-paper and fitted with a conical cap of strong paper, in which the acid collects.[2] According to Wöhler, the gum benzoin is dissolved in an equal volume of absolute alcohol and fuming hydrochloric acid added to the hot solution until the resin commences to separate out; it is then distilled, water being added at intervals, and the distillate, which contains ethyl benzoate, warmed with caustic potash and then heated to boiling and saturated with hydrochloric acid. Benzoic acid separates out on cooling and is found to possess precisely the same smell as the sublimed acid.[3]

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[1] Gal, *Ber. Deutsch. Chem. Ges.* vi. 824.
[2] Ducheek, *Gmelin's Org. Chem.* v. 332.
[3] Loew, *Journ. Prakt. Chem.* [2] xix. 312.
[4] Wöhler, *Ann. Chem. Pharm.* lxvii. 360.
[5] Seligsohn, *Chem. Centralbl.* 1861, 241.
[6] *Schulze, Ber. Deutsch. Chem. Ges.* xviii. 615.

In order to extract the acid from the resin by Scheele's method, it is well mixed with an equal weight of slaked lime, repeatedly boiled out with water, the filtrate evaporated to one-sixth of its original bulk, treated with bleaching-powder solution, and then boiled with hydrochloric acid until all the chlorine has been removed. The acid separates out on cooling and is re-crystallized from hot water.[4]

It is prepared from the urine of cows or horses by allowing it to stand for several days, clarifying with milk of lime, evaporating the liquid to one-fourth of its bulk and precipitating the benzoic acid with hydrochloric acid. Since the evaporation produces a very unpleasant smell, it is better to precipitate the excess of lime by carbonic acid and add ferric chloride, to precipitate ferric benzoate, which is then decomposed by hydrochloric acid. The acid thus obtained is purified by being redissolved in milk of lime with the addition of a little bleaching-powder solution, separated by hydrochloric acid and re-crystallized from hot water. The final product (*acidum benzoicum ex urina*) still smells of urine, and is not employed for pharmaceutical purposes. The smell may, however, be disguised by the addition of some of the sublimed acid. About two kilos. of acid are obtained from 1,000 kilos. of urine.[5]

P. and E. Depouilly have proposed to obtain benzoic acid from phthalic acid,[6] which is obtained by the oxidation of naphthalene and is now manufactured on the large scale. When its calcium salt is heated to 330°—350° with slaked lime in absence of air, calcium benzoate and calcium carbonate are formed :

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[1] Jacobsen found in it methyl benzoate, benzyl benzoate, vanillin, guiacol, catechol and other aromatic compounds (*Ber. Deutsch. Chem. Ges.* xvii. Ref. 354).

[2] Mohr, *Ann. Chem. Pharm.* xxix. 117; Löwe, *Journ. Prakt. Chem.* cviii. 257.

[3] *Ann. Chem. Pharm.* xlix. 245.

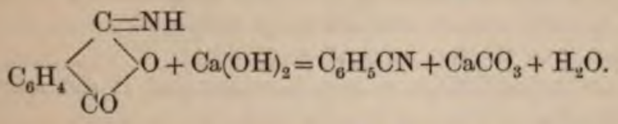
[4] Stenhouse.

[5] Hofmann, *Ber. Entw. Chem. Ind.* ii. 431.

[6] *Jahresb. Chem.* 1865, 328.

$$2C_6H_4(CO_2)_2Ca + Ca(OH)_2 = (C_6H_5.CO_2)_2Ca + 2CO_3Ca.$$

According to the method of Laurent and Castelhaz,[1] acid ammonium phthalate is converted into phthalimide by heating, and this is then distilled with lime, benzonitril being formed :



$$C_6H_4\left\langle\begin{matrix}C{=}NH\\CO\end{matrix}\right\rangle O + Ca(OH)_2 = C_6H_5CN + CaCO_3 + H_2O.$$

The benzonitril is then converted into benzoic acid by boiling with caustic soda solution.

Benzoic acid is now generally prepared from toluene ; this may be simply oxidized by boiling with dilute nitric acid, but it is more advantageous to first convert it into benzyl chloride,[2] and then boil 100 parts of this with 300 parts of nitric acid of sp. gr. 1·313 and 200 parts of water for about ten hours in an apparatus connected with an inverted condenser, until the smell of benzyl chloride and benzaldehyde has disappeared, and the liquid solidifies on cooling to a crystalline mass, no oily drops being formed.[3]

This method, according to A. von Rad, is not adapted for the preparation of the acid on the large scale ; it can, however, be readily obtained by heating benzotrichloride or benzenyl chloride with water under pressure :[4]

$$C_6H_5.CCl_3 + 2H_2O = C_6H_5.CO_2H + 3HCl.$$

Since it is difficult to prepare pure benzenyl chloride, the acid obtained always contains chlorine substitution products, which adhere to it very obstinately.

Espenschied proposes to boil benzenyl chloride with milk of lime or caustic soda and whitening, and then to proceed as in the preparation of benzaldehyde from benzal chloride (p. 136).

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[1] *Jahresb. Chem.* 1868, 459.

[2] Grimaux and Lauth, *Bull. Soc. Chim.* vii. 100.

[3] Lunge and Petri, *Ber. Deutsch. Chem. Ges.* x. 1275.

[4] *Dingler's Polyt. Journ.* ccxxxi. 538.

Jacobsen obtains benzoic acid, together with acetyl chloride, by heating benzenyl chloride with glacial acetic acid and some zinc chloride:

$$C_6H_5.CCl_3 + 2CH_3.CO.OH = C_6H_5.CO.OH + 2CH_3.COCl + HCl$$

In order to avoid the evolution of hydrochloric acid, which carries off acetyl chloride with it, half of the acetic acid is replaced by zinc acetate.

Benzoic acid can also be prepared without the formation of acetyl chloride, by heating benzenyl chloride with a little acetic acid and zinc acetate, and gradually adding the amount of water necessary for the formation of the acid.[1]

Since benzaldehyde is now manufactured, it can readily be employed as a source of benzoic acid.

2096 *Properties.*—It crystallizes in lustrous, flat, monoclinic plates or needles; by the gradual evaporation of its solution it is obtained in larger tablets, which however are always thin, while when Guichard allowed a mixture of benzoin resin and carbon disulphide to stand for a long time, tolerably large crystals were formed, which had exactly the appearance of crystals of gypsum.[2]

Benzoic acid has a sharp acid taste and produces a peculiar irritation in the throat; it melts at 121·4°, and boils at 249° (Kopp), but volatilizes at 100°, and sublimes rapidly at 140°. It also volatilizes with steam, one gramme passing over with two litres of water (Nölting). Its vapour has an aromatic, penetrating odour, produces coughing and attacks the eyes violently, more mildly when it is mixed with steam. The specific gravity of its vapour is, according to Mitscherlich, 4·27; according to C. and V. Meyer, who determined it in diphenylamine vapour, it is 4·24,[3] the calculated number being 4·229.

1,000 parts of water dissolve:[4]

at	0	10	20	30	40	50	60	70	80	90	100°
	1·70	2·10	2·90	4·10	5·55	7·75	11·55	17·75	27·15	40·75	58·75

parts of the acid.

100 parts of absolute ether at 15° dissolve 31·35 parts; 100 parts of 40 per cent. alcohol, 41·62 parts; and 100 parts of

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[1] *Ber. Deutsch. Chem. Ges.* xiii. 2013.

[2] *Ibid.* vi. 453.

[3] *Ibid.* xi. 2258.

[4] Bourgoin, *Ann. Chim. Phys.* [5] xv. 168.

absolute alcohol, 46·68 parts of benzoic acid;[1] boiling alcohol dissolves about twice this quantity. It also readily dissolves in chloroform, carbon disulphide, volatile and fatty oils and concentrated sulphuric acid.

It is characteristic of benzoic acid that certain impurities, even when they are present in extremely small quantities, alter its physical properties to a very considerable extent; so largely in fact, that the impure acid has been mistaken for an isomeride. Thus, E. Kopp, by the oxidation of gum benzoin with dilute nitric acid, obtained the amorphous parabenzoic acid as a white powder, which melts at 113°; it is converted into ordinary benzoic acid by distillation.[2] Another so-called isomeric acid was named salylic acid by Lautemann and Kolbe, because they had obtained it from salicylic acid, $C_6H_4(OH)COOH$.[3] The latter was converted into a chlorine compound by phosphorus pentachloride and this was decomposed by water into hydrochloric acid and chlorosalylic acid or orthochlorobenzoic acid, $C_6H_4Cl.CO_2H$. Salylic acid was obtained from this by the action of water and sodium amalgam. This compound crystallizes from hot water in indistinct needles or small plates, which, on drying, form an odourless sandy powder, while the soft, light plates of benzoic acid have a faint but distinct aromatic odour. When its aqueous solution is boiled, however, the characteristic smell becomes perceptible. It melts at a lower temperature than benzoic acid, from which it also differs in fusing when heated with a quantity of water insufficient to dissolve it, and in the fact that its hot, saturated solution becomes milky on cooling and then again clear, crystalline flocks being deposited. Its salts also differ from the benzoates in crystalline form and in solubility.

Kekulé confirmed these results,[4] and Griess obtained a substance which he found to be identical with salylic acid, by decomposing azo-amidobenzoic acid suspended in boiling alcohol with nitrogen trioxide.[5] Kolbe and Lautemann put forward the suggestion that the isomerism of these acids was due to a difference between their radicals,[6] but Cannizzaro showed that on distillation with caustic baryta they both yield the same substance, viz., benzene.[7]

The two acids were then assumed to be physical isomerides, until Reichenbach and Beilstein showed that salylic acid is nothing but a more or less impure benzoic acid.[1] If the acid obtained from salicylic acid be subjected to distillation with steam, a perfectly pure benzoic acid passes over which possesses the correct melting-point and all the characteristic properties. Kolbe has confirmed this result, and finds that his salylic acid contains a small quantity of a yellow, resinous substance, which is not volatile in steam. When some of this is added to a hot, saturated solution of pure benzoic acid, the liquid on cooling deposits crystals of salylic acid. The admixed substance can be destroyed by the addition of potassium permanganate to the hot solution.[2]

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[1] Bourgoin; *Bull. Soc. Chim.* xxix. 242.

[2] *Compt. Rend. Chim.* 1849, 154.

[3] *Ann. Chem. Pharm.* cxv. 187.

[4] *Ibid.* cxvii. 158.

[5] *Ibid.* cxvii. 34.

[6] *Ibid.* cxv. 169.

[7] *Ibid.* Suppl. i. 247.

The salylic acid obtained from azo-amidobenzoic acid contains a little nitrobenzoic acid, as does the benzoic acid which is prepared by the oxidation of toluene with dilute nitric acid.[3] When this acid is distilled, a trace of the nitro-compound volatilizes with it and prevents it from crystallizing well, while when a little of the nitro-compound is added to a hot saturated solution of pure benzoic acid, it becomes milky on cooling and deposits flocks, which are much more soluble than the pure acid and melt at a lower temperature. Pure benzoic acid cannot be prepared from this either by sublimation or re-crystallization, but the impurity can readily be removed by dissolving in concentrated ammonia, saturating with sulphuretted hydrogen, heating to boiling, and then evaporating off the ammonium sulphide on the water-bath. Hydrochloric acid now precipitates pure benzoic acid, while amidobenzoic acid remains in solution (Reichenbach and Beilstein).

An admixture of cinnamic acid, which melts at 133·3°, also lowers the melting-point of benzoic acid considerably,[4] so that a mixture of equal parts of the two acids melts at 84·3°, an excess of either acid raising the melting-point.[5]

Benzoic acid is employed in the manufacture of colouring matters and in medicine. It has antiseptic properties, but exerts a more feeble action than salicylic acid.[6] The observation that cranberries withstand fermentation and putrefaction better than most other fruits, gave the clue to the discovery of benzoic acid in them.

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[1] *Ann. Chem. Pharm.* cxxxi. 309.
[2] *Journ. Prakt. Chem.* [2] xii. 151.
[3] Fittig, *Ann. Chem. Pharm.* cxx. 214.
[4] Kolbe and Lautermann, *Ann. Chem. Pharm.* cxix. 136.
[5] Kachler, *Ber. Deutsch. Chem. Ges.* ii. 515.
[6] Kolbe and v. Meyer, *Journ. Prakt. Chem.* [2] xxii. 133, 178.

2097 When benzoic acid is distilled with slaked lime or caustic baryta, it is decomposed into benzene and carbon dioxide (Mitscherlich). It also undergoes this decomposition when heated with caustic soda,[1] and when its vapour is passed over heated pumice stone[2] or iron.[3] Some diphenyl is always formed in this way, and at a very high temperature the acid is decomposed with separation of graphite and formation of carbonic oxide, carbon dioxide, hydrogen and diphenyl, $C_{12}H_{10}$.[4] When its vapour is passed over heated zinc-dust, it is reduced to benzaldehyde.[5] Sodium amalgam reduces its boiling solution with formation of benzaldehyde, benzyl alcohol, a crystalline compound, $C_{14}H_{14}O_2$, and benzoleic acid, $C_7H_{10}O_2$,[6] which is further described below. On heating with concentrated hydriodic acid to 275°—280°, it is first reduced to toluene, but heptane and hexane are formed on further heating, the latter being derived from the benzene, which is formed by the decomposition of the acid.[7]

It is not attacked by chromic acid solution; ozone converts it in alkaline solution into carbon dioxide and water.[8] It is converted in the animal organism into hippuric acid and appears in this form in the urine;[9] a portion is simultaneously oxidized to succinic acid, which is also formed when an aqueous solution of benzoic acid is treated with lead dioxide and sulphuric acid.[10] On oxidation with manganese dioxide and sulphuric acid, Carius obtained carbon dioxide, formic acid, and some phthalic acid,[11] while Oudemans also detected a small quantity of the isomeric terephthalic acid.[12] When the solution of its calcium salt is electrolyzed, the acid is not decomposed in a similar manner to the fatty acids, but the nascent oxygen exerts an oxidizing action, with formation of carbon dioxide, carbonic oxide, and some acetylene.[13]

Benzoleic acid, or *Hydrobenzoic acid*, $C_7H_{10}O_2$, is formed when sodium amalgam is allowed to act on a boiling solution of benzoic acid, hydrochloric acid being added at intervals benzyl alcohol and a crystalline substance, $C_{14}H_{14}O_2$,[1] are simultaneously formed. Otto obtained the same acid from hydrobenzuric acid,[2] and, together with other compounds, by the action of sodium amalgam on benzoyl-glycollic acid (p. 165).[3] It is an oily liquid, which has a repulsive odour resembling that of valerianic acid, and is rapidly altered in the air. When hydrochloric acid is passed into its alcoholic solution, the ethyl ether is formed and resembles ethyl valerate, but has a sharper smell; in the air the smell becomes exceedingly disagreeable, and, since it clings persistently to the clothes, increases the difficulty of the investigation of the compound and the free acid.

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[1] Barth and Schreder, *Ber. Deutsch. Chem. Ges.* xii. 2555.
[2] Barreswill and Boudault, *Journ. Pharm. Chim.* v. 265.
[3] F. d'Arcet, *Journ. Prakt. Chem.* xiii. 427.
[4] Schulz, *Ann. Chem. Pharm.* clxxiv. 202.
[5] Baeyer, *ibid.* cxl. 295.
[6] Kolbe, *ibid.* cxviii. 122; Herrmann, *ibid.* cxxxii. 75.
[7] Berthelot, *Jahresb. Chem.* 1867, 364.
[8] Gorup-Besanez, *Ann. Chem. Pharm.* cxxv. 207.
[9] Wöhler, *Berzelius' Lehrb.* Ed. 4, iv. 376; see also hippuric acid.
[10] Meissner and Shepard, *Jahresb. Chem.* 1866, 397.
[11] *Ann. Chem. Pharm.* cxlviii. 72.
[12] *Zeitschr. Chem.* 1869, 84.
[13] Berthelot, *Bull. Soc. Chim.* [2] ix. 103; Bourgoin, *ibid.* 431.

SALTS AND ETHERS OF BENZOIC ACID.

2098 Benzoic acid decomposes carbonates in aqueous solution, but when a current of carbon dioxide is passed into an alcoholic solution of potassium benzoate, potassium carbonate separates out. Most of the benzoates are soluble in water and alcohol; some, such as the sodium and barium salts, are withdrawn from their solutions by animal charcoal, and calcium benzoate is decomposed by it, so that free benzoic acid can be extracted by ether.[4]

Potassium benzoate, $C_7H_5KO_2 + 3H_2O$, crystallizes with difficulty in small plates which effloresce in the air and are very soluble in water and alcohol.

Sodium benzoate, $C_7H_5NaO_2 + H_2O$, crystallizes in needles, which also effloresce in the air and are very soluble in alcohol. It is used in medicine.

Ammonium benzoate, $C_7H_5(NH_4)O_2$, separates from a solution containing an excess of ammonia in deliquescent rhombic crystals; it is also employed medicinally. Large crystals of the less soluble acid salt, $C_7H_5(NH_4)O_2 + C_7H_6O_2$, are obtained by the gradual evaporation of its aqueous solution (Berzelius).

Calcium benzoate, $(C_7H_5O_2)_2Ca + 2H_2O$, crystallizes from hot water in long lustrous needles which form fascicular aggregates; they dissolve in 29 parts of cold water and effloresce in the air.

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[1] Herrmann, *Ann. Chem. Pharm.* cxxxii. 75.

[2] *Ibid.* cxxxiv. 115.

[3] *Ibid.* cxlv. 350.

[4] L. Liebermann, *Ber. Wien. Akad.* 1877, 331.

Barium benzoate, $(C_7H_5O_2)_2Ba + 3H_2O$, is only slightly soluble in water, and crystallizes in needles or hard, lustrous tablets.

Lead benzoate, $(C_7H_5O_2)_2Pb + H_2O$, is obtained by the addition of lead acetate to a solution of the potassium salt; it is a crystalline, difficultly soluble precipitate.

Copper benzoate, $(C_7H_5O_2)_2Cu + 2H_2O$, crystallizes in light blue plates united in spherical masses or in needles.

Silver benzoate, $C_7H_5AgO_2$, is a curdy precipitate, which is soluble in alcohol and crystallizes from hot water in flat needles.

Mercuric benzoate, $(C_7H_5O_2)_2Hg + H_2O$, crystallizes from hot water in needles which are almost insoluble in cold water.

Ferric benzoate, $(C_7H_5O_2)_6Fe_2$. Berzelius obtained this salt in yellow needles by dissolving ferric hydroxide in aqueous benzoic acid; it is decomposed by water and alcohol with formation of an insoluble basic salt. Sestini was unable to prepare this compound.[1] When a soluble benzoate is added to neutral ferric chloride, a reddish yellow precipitate is thrown down, which is decomposed by washing with water into a soluble acid salt and an insoluble basic salt. If the iron solution has been previously treated with sufficient ammonia to produce a dark red colouration, soluble benzoates give a voluminous, hydrated, flesh-coloured precipitate of $(C_7H_5O_2)_3Fe_2(OH)_3$, which is not altered by cold water.

These reactions are employed for the separation of iron from manganese and for the detection of benzoic acid and its separation from other acids.

Methyl benzoate, $C_6H_5.CO.OCH_3$, is best prepared by passing hydrochloric acid into a solution of benzoic acid in methyl alcohol, distilling, and then precipitating the ether with water.[2] It is a liquid which possesses an aromatic odour and boils at 199°.

Ethyl benzoate was prepared by Scheele as long ago as 1785, by the distillation of a mixture of alcohol, benzoic acid and hydrochloric acid. It is not formed when an alcoholic solution of the acid is allowed to stand in the cold, but the ether is gradually formed if a little hydrochloric acid be added, or if the liquid be heated to 100°. In order to prepare it, the method adopted for the preparation of the methyl ether may be followed, or the alcoholic solution of the acid may be heated with sulphuric or hydrochloric acid. It is a liquid which has a pleasant aromatic smell, and boils at 213°.

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[1] *Zeitschr. Chem* iv. 668.

[2] Carius, *Ann. Chem. Pharm.* cx. 210.

Ethyl benzoate is also readily formed by the action of benzoyl chloride on alcohol (Wöhler and Liebig), which is more readily attacked by it than water. The presence of alcohol even in very dilute aqueous solution can therefore be detected by warming it with a little benzoyl chloride and removing the excess of this by caustic soda; even when only 0·1 per cent. of alcohol is present, the characteristic smell of ethyl benzoate can be distinctly recognized (Berthelot; see Part I. p. 318).

	Boiling-point.
Isopropyl benzoate,[1] $C_6H_5.CO.OCH(CH_3)_2$.	218°
Propyl benzoate,[2] $C_6H_5.CO.OC_3H_7$ . . .	229·5°
Butyl benzoate,[3] $C_6H_5.CO.OC_4H_9$ . . .	247·3°
Amyl benzoate,[4] $C_6H_5.CO.OC_5H_{11}$ . . .	260·7°
Octyl benzoate,[5] $C_6H_5.CO.OC_8H_{17}$ . . .	306°
Allyl benzoate,[6] $C_6H_5.CO.OC_3H_5$ . . .	228°

Benzyl benzoate, $C_6H_5.CO.OCH_2.C_6H_5$. Cannizzaro obtaine this compound by the distillation of benzyl alcohol with benzo chloride or benzoic anhydride.[7] It boils at 323°—324°, has t sp. gr. of 1·1227 at 19°, and solidifies in a freezing mixture lustrous, compact crystals, melting at 21°.[8] As already mention it is also formed by the action of sodium methylate on be aldehyde (p. 93) and is a constituent of Peru balsam[9] and Tolu balsam,[10] but has not yet been obtained from them in pure state. If the ether be submitted to distillation while it s contains water, it is decomposed with formation of benzoic ac benzyl alcohol and toluene.

Ethylene benzoate, $(C_6H_5.CO_2)_2C_2H_4$. Wurtz prepared t compound by the action of silver benzoate on ethyle bromide;[11] it crystallizes from ether in lustrous, rhombic prisms melting at 67°.

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[1] Silva, *Ann. Chem. Pharm.* cliv. 255.
[2] Linnemann, *ibid.* clxi. 28.
[3] *Ibid.* clxi. 92.
[4] Rieckher, *ibid.* lxiv. 336.
[5] Zincke, *ibid.* clii. 7.
[6] Hofmann and Cahours, *ibid.* c. 358; cii. 297.
[7] *Ibid.* xc. 254.
[8] L Claisen, private communication.
[9] Kraut, *Ann. Chem. Pharm.* clii. 129; *Ber. Deutsch. Chem. Ges.* ii. 18.
[10] Busse, *ibid.* ix. 830.
[11] *Jahresb. Chem.* 1859, 676.
[12] Bodewig, *ibid.* 1879, 676

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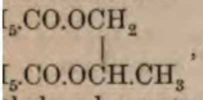
ollowing propylene ethers have been prepared in a nanner:

Melting-point.

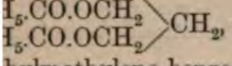
ene benzoate:[1]



$$\begin{array}{l}\mathrm{I_5.CO.OCH_2} \\ \qquad | \\ \mathrm{I_5.CO.OCH.CH_3}\end{array}$$

, viscous fluid . . . . . —

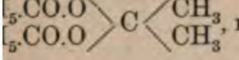
thylene benzoate:[2]



$$\left.\begin{array}{l}\mathrm{I_5.CO.OCH_2} \\ \mathrm{I_5.CO.OCH_2}\end{array}\right\rangle \mathrm{CH_2}$$

, scaly crystals . . . . 53°

hylmethylene benzoate:[3]



$$\left.\begin{array}{l}\mathrm{I_5.CO.O} \\ \mathrm{I_5.CO.O}\end{array}\right\rangle \mathrm{C} \left\langle\begin{array}{l}\mathrm{CH_3} \\ \mathrm{CH_3}\end{array}\right.$$

, monoclinic pyramids . 69—71°

st of these yields acetone on saponification.

lene benzoate, $(C_6H_5.CO.O)_2CH.C_6H_5$, is formed by the benzidene chloride on silver benzoate, and crystallizes arent prisms, melting at 50°.[4]

enzoic ethers of glycerol, erythrol, mannitol, the glucoses, e also been prepared.[5]

Phenyl benzoate, $C_6H_5.CO.OC_6H_5$. Ettling and Sten- served a compound among the distillation products of enzoate which they named benzoic oxide, C_7H_5O,[6] while considered it to be the radical benzoyl.[7] List and it then found that it has the formula $C_{13}H_{10}O_2$, and is sed by alcoholic potash into benzoic and carbolic acids, is a compound of benzoic acid and phenyl oxide.[8] They howed that it is identical with the benzophenide, which and Gerhardt obtained by the action of benzoyl chloride l.[9]

l benzoate is readily formed when benzoyl chloride is ith phenol until hydrochloric acid ceases to be evolved, when phenol is heated with benzamide.[10] It is readily a alcohol and ether, and crystallizes from a mixture of lustrous, monoclinic prisms,[11] which melt at 71° and at a higher temperature. Its smell resembles that of

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and Crafts, *Zeitschr. Chem.* 1871, 489; Mayer, *Ann. Chem. Pharm.* 5.

, *Ann. Chim. Phys.* [5] xiv. 500.

ieim, *Ann. Chem. Pharm.* Suppl. vi. 360; Friedel and Ladenburg, 195.

ardt, *Jahresber. Chem.* 1857, 471; Wicke, *Ann. Chem. Pharm.* cii. 356.

lot, *ibid.* lxxxviii. 311; xcii. 302; *Jahresber.* 1855, 677; 1856, 660;

Chem. Pharm. liii. 77, 94.

[7] *Ibid.* lxxxvii. 162.

c. 190.

[9] *Ibid.* lxxv. 75; lxxxvii. 161.

chi, *ibid.* clxxi. 141.

[11] Bodewig, *Jahresber.* 1879, 675.

the geranium. Chlorine and bromine effect substitution in the phenyl and not in the benzoyl group.

Trinitrophenyl benzoate, $C_6H_5.CO.OC_6H_2(NO_2)_3$. Gerhardt and Laurent prepared this compound by heating picric acid with benzoyl chloride. It is insoluble in water, slightly soluble in cold, more readily in hot alcohol, and crystallizes in lustrous, golden-yellow, rhombic plates, which detonate when heated.[1]

Cresyl benzoate, $C_6H_5.CO.OC_6H_4.CH_3$. The three isomeric ethers have been prepared by Engelhardt and Latschinow.[2]

	Melting-point.	Boiling-point.
Orthocresyl benzoate, oily liquid . . .	—	—
Metacresyl benzoate, crystals	38°	290°—300°
Paracresyl benzoate, six-sided tablets .	70°	—

Phenylene benzoate, $(C_6H_5.CO.O)_2C_6H_4$, is also known in three isomeric forms, which are obtained from the dihydroxybenzenes.

	Melting-point.
Dibenzoylcatechol, rhombic crystals[3] . . .	—
Dibenzoylresorcinol, scales[4]	117°
Dibenzoylquinol, silky needles[5]	199°

Tribenzoylphloroglucinol, $(C_6H_5.CO.O)_3C_6H_3$, forms small, lustrous scales, which are almost insoluble in alcohol.[6] The benzoic ether of pyrogallol, according to Malin, does not crystallize, but its dimethyl ether, and two homologues of the latter which occur in the higher boiling portions of beech-wood-tar oil, give very characteristic ethereal salts of benzoyl.[7] Since these three ethereal salts, which are very similar in their properties, can be separated by means of their different solubilities, they will be mentioned here:

	Melting-point.
Benzoylpyrogallol dimethyl ether: $C_6H_5.CO.OC_6H_3(OCH_3)_2$	118°
Benzoylmethylpyrogallol dimethyl ether: $C_6H_5.CO.OC_6H_2(CH_3)(OCH_3)_2$	118°—119°
Benzoylpropylpyrogallol dimethyl ether: $C_6H_5.CO.OC_6H_2(C_3H_7)(OCH_3)_2$ . . .	91°

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[1] *Ann. Chem. Pharm.* lxxv. 77.

[2] *Zeitschr. Chem.* 1869, 615; see also Kekulé, *Ber. Deutsch. Chem. Ges.* vii. 1007; Guareschi, *Ann. Chem. Pharm.* clxxi. 142.

[3] Nachbauer, *ibid.* cvii. 243.

[4] Malin, *ibid.* cxxxviii. 76; Döbner, *Ber. Deutsch. Chem. Ges.* xi. 2269.

[5] Döbner and Wolff, *ibid.* xii. 661.

[6] Hlasiwetz and Pfaundler, *Ann. Chem. Pharm.* cxix. 199.

[7] Hofmann, *Ber. Deutsch. Chem. Ges.* xii. 1373.

Quinonoxime benzoate, $C_6H_4O(NO.CO.C_6H_5)$, is formed when benzoyl chloride is added to sodium quinonoximate (Part III. p. 172), which is covered with pure ether or chloroform. It crystallizes in yellowish needles, which melt with decomposition at 168°—175°, and give Liebermann's reason with phenol and sulphuric acid.[1]

2100 *Benzoyl-glycollic acid*, $C_6H_5.CO.OCH_2.CO_2H$, has hitherto only been prepared from hippuric acid or benzoylamido-acetic acid, by treating it with nitrous acid,[2] or by passing chlorine into its dilute alkaline solution.[3] It crystallizes from hot water in thin tablets or large prisms, and decomposes on boiling with water, or more rapidly with dilute mineral acids, into benzoic and glycollic acids. Otto, by the action of sodium amalgam on its aqueous solution, obtained benzoleic acid (p. 159) and two other isomeric acids which have not yet been thoroughly investigated.

Ethyl benzoyl-glycollate, $C_6H_5.CO.OCH_2.CO_2C_2H_5$. Andrejew obtained this substance by heating ethyl chloracetate with sodium benzoate; it is a liquid which boils at 277°—279°, and decomposes into alcohol, benzoic acid and glycollic acid, when boiled with alcoholic potash.[4]

Benzoyl-lactic acid, $CH_3(CH.O.CO.C_6H_5)CO_2H$, is formed when lactic acid is heated to 180° with benzoic acid,[5] as well as by the action of benzoyl chloride on lactic acid or calcium lactate.[6] It separates from a hot, aqueous solution in tablets or needles, melting at 112°. On boiling with water or a dilute acid it is decomposed into lactic and benzoic acids.

Ethyl benzoyl-lactate, $C_{10}H_9O_4.C_2H_5$, is formed by the action of benzoyl chloride on ethyl lactate, and by heating silver benzoyl-lactate with ethyl iodide. It is a liquid which boils at 288°, and is decomposed into lactic acid and ethyl benzoate by heating with water to 150°.

Benzoyl compounds of tartaric and racemic acids have also been prepared.[7]

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[1] Walker, *Ber. Deutsch. Chem. Ges.* xvii. 399.

[2] Strecker, *Ann. Chem. Pharm.* lxviii. 54; Strecker and Sokolow, *ibid.* lxxx. 17.

[3] Gössmann, *ibid.* xcix. 181.

[4] *Ibid.* cxxxiii. 284.

[5] Strecker and Sokolow, *loc. cit.*; Strecker, *ibid.* xci. 359.

[6] Wislicenus, *ibid.* cxxxiii. 264.

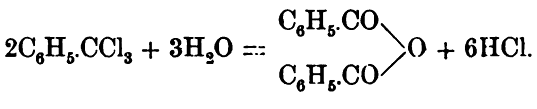
[7] Dessaignes, *Jahresber.* 1857, 307; Perkin, *Ann. Chem. Pharm.* Suppl. v. 274; Anschütz and Pictet, *Ber. Deutsch. Chem. Ges.* xiii. 1178.

OXIDES OF BENZOYL.

2101 *Benzoyl oxide*, or *Benzoic anhydride*, $(C_6H_5.CO)_2O$, was discovered by Gerhardt in 1853. He first prepared it by heating benzoyl chloride with sodium benzoate, and named it anhydrous benzoic acid or benzoyl benzoate;[1] he subsequently found that it can be more simply obtained by the action of phosphorus oxychloride on an excess of sodium benzoate, a portion of this being simultaneously converted into benzoyl chloride.[2] Phosphorus pentachloride[3] or chloride of sulphur[4] may be employed instead of phosphorus oxychloride. It is also formed in small quantity when benzoic acid is heated with phosphorus pentoxide,[5] and in larger amount by heating benzoyl chloride to 140°—150° with barium oxide,[6] or to 160°—220° with benzoic acid.[7] Gerhardt had already found that it may easily be obtained by the action of benzoyl chloride on potassium oxalate:

$$K_2C_2O_4 + 2C_6H_5.COCl = (C_6H_5.CO)_2O + 2KCl + CO + CO_2.$$

Anhydrous oxalic acid may be advantageously employed instead of the potassium salt; the reaction takes place at 50°—60° accompanied by a regular evolution of gas, and 80 per cent. of the theoretical yield is obtained, together with some unattacked chloride and benzoic acid.[8] Finally, it can also be obtained by heating benzenyl trichloride with silver oxide, or with concentrated sulphuric acid containing 4·6 per cent. of water:[9]



$$2C_6H_5.CCl_3 + 3H_2O = \begin{matrix} C_6H_5.CO \\ C_6H_5.CO \end{matrix}\!\!>O + 6HCl.$$

Anhydrous oxalic acid may be substituted for the sulphuric acid:[10]

$$2C_6H_5.CCl_3 + 3C_2O_4H_2 = (C_6H_5.CO)_2O + 3HCl + 3CO + 3CO_2.$$

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[1] *Ann. Chem. Pharm.* lxxxii. 127.
[2] *Ibid.* lxxxvii. 73.
[3] Wunder, *Journ. Prakt. Chem.* lxi. 280.
[4] Heintz, *Pogg. Ann.* xcviii. 458.
[5] Etard and Gal, *Bull. Soc. Chim.* xxv. 342.
[6] Gal, *Ann. Chem. Pharm.* cxxviii. 127.
[7] Anschütz, *Ber. Deutsch. Chem. Ges.* x. 1882.
[8] *Ibid.*
[9] Janssen, *ibid.* xii. 1495, Patent 30 Oct. 1878 (No. 6689).
[10] Anschütz, *ibid.* ccxxvi. 20.

Benzoic anhydride crystallizes in rhombic prisms (Bodewig), melting at 42°; it boils at 360° (Anschütz), and is tolerably soluble in alcohol and ether. It is scarcely attacked by cold water, but when heated with water it gradually forms benzoic acid, and with alcohol, ethyl benzoate. When heated in a stream of hydrochloric acid, it decomposes into benzoyl chloride and benzoic acid.[1] Chlorine and bromine exert a similar action, substitution products being simultaneously formed.

Benzoyl acetyl oxide, $CH_3.CO.O.CO.C_6H_5$. Gerhardt prepared this compound by the action of acetyl chloride on sodium benzoate, and named it *anhydrous benzoic acetic acid.*[2] It is a heavy, oily liquid, which has a pleasant smell like that of Spanish wine, is gradually attacked by water, more rapidly by alkalis, and is completely decomposed by distillation into benzoic anhydride and acetic anhydride.[3] It is also formed when benzoic acid is heated to 220° with acetic anhydride.[4] According to Loir, an anhydride is obtained by the action of benzoyl chloride on sodium acetate, which differs from that prepared by Gerhardt's method in yielding acetyl chloride when heated with hydrochloric acid to 130°, while Gerhardt's compound is first attacked at 160°, with formation of benzoyl chloride.[5] This, however, is inaccurate, and Greene has shown that the compound, in whatever way it is prepared, behaves in exactly the same manner towards hydrochloric acid, the same products—acetyl chloride and acetic acid, benzoyl chloride and benzoic acid—being formed as in the case of the anhydrides themselves.[6]

A number of other mixed anhydrides are now known, which, like the foregoing, decompose on distillation into benzoic anhydride and another simple anhydride,[7] and must therefore be looked upon rather as mixtures than definite compounds.

Benzoyl dioxide, or *Benzoyl peroxide*, $(C_6H_5.CO)_2O_2$, was prepared by Brodie by the action of benzoyl chloride on barium dioxide; it separates from ether or carbon disulphide in rhombic crystals, which melt at 103·5°, detonate when more strongly heated, and when boiled with caustic potash are converted into benzoic acid with evolution of oxygen.[8]

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[1] Mosling, *Ann. Chem. Pharm.* cxviii. 303.

[2] *Ibid.* lxxxvii. 81.

[3] Anschütz, *ibid.* ccxxvi. 12.

[4] *Ibid.*

[5] *Ann. Chim. Phys.* [5] xviii. 132.

[6] *Bull. Soc. Chim.* xxxiii. 424.

[7] Gerhardt, *Ann. Chem. Pharm.* lxxxii. 127; lxxxvii. 163; Chiozza, *ibid.* lxxxiv. 106; lxxxvi. 259; Chiozza and Malerba, *ibid.* xci. 102.

[8] *Ann. Chem. Pharm.* cviii. 80; Lippmann, *Monatsh. Chem.* v. 560.

HALOGEN COMPOUNDS OF BENZOYL.

2102 *Benzoyl chloride*, $C_6H_5.COCl$, was discovered in 1832 by Wöhler and Liebig; they obtained it by the action of dry chlorine on pure oil of bitter almonds, and describe it as a transparent liquid the vapour of which violently attacks the eyes, and has a peculiar, very penetrating odour resembling the sharp smell of horse-radish.[1] Cahours then prepared it by the action of phosphorus pentachloride on benzoic acid,[2] Gerhardt by that of phosphorus oxychloride on sodium benzoate,[3] and Béchamp by heating benzoic acid with phosphorus trichloride.[4] Friedel subsequently observed its formation when hydrochloric acid is passed over a mixture of benzoic acid and phosphorus pentoxide heated to 200°,[5] this being an important general method for the formation of acid chlorides. Harnitz-Harnitzky stated that it might also be obtained by exposing a mixture of carbonyl chloride and benzene vapour to the action of sunlight,[6] but Berthelot was unable to confirm this statement,[7] although it is undoubtedly formed in this way when aluminium chloride is present, (p. 30).[8]

It also may be obtained by heating benzenyl trichloride with anhydrous oxalic acid:

$$C_6H_5.CCl_3 + C_2O_4H_2 = C_6H_5.COCl + 2HCl + CO_2 + CO.$$

Benzoic anhydride is also formed in this reaction. In order to prepare the chloride, a mixture of two molecules of phosphorus trichloride with three molecules of benzoic acid is heated until hydrochloric acid ceases to be evolved, water is then added and the oily liquid which separates purified by distillation; according to another method, benzoic acid is heated with one molecule of phosphorus pentachloride, and the mixture distilled, the distillate consisting at first of phosphorus oxychloride mixed with a little benzoyl chloride, followed by pure benzoyl chloride. The phosphorus oxychloride is then employed for a further preparation by being heated with sodium benzoate, an excess of which must be avoided, as, otherwise, some benzoic anhydride would be formed. The crude chloride, prepared by either of these methods, is freed from adhering chlorides of phosphorus by treatment with cold water, and is then purified by distillation.

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[1] *Monatsh. Chem.* iii. 262.

[2] *Ibid.* lx. 251.

[3] *Ibid.* lxxxvii. 63.

[4] *Journ. Prakt. Chem.* lxviii. 489.

[5] *Bull. Soc. Chim.* ii. 80.

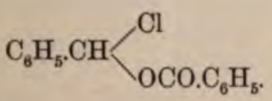
[6] *Ann. Chem. Pharm.* cxxxii. 72.

[7] *Bull. Soc. Chim.* xiii. 9, 392.

[8] Ador, Crafts and Friedel, *Ber. Deutsch. Chem. Ges.* x. 1854.

Properties.—It is a strongly refractive liquid, which fumes in the air, has a sp. gr. of 1·2324 at 0° and solidifies when cooled in crystals melting at —1°. It boils at 198°; its vapour attacks the lungs and mucous membrane very violently. It is gradually decomposed by cold, more rapidly by hot water, with formation of benzoic and hydrochloric acids; it is rapidly converted into ethyl benzoate by alcohol, and the other alcohols produce a similar reaction. Since it undergoes double decomposition so readily, it is largely employed for the preparation of other benzoyl derivatives; many examples of this have been already given and others will be met with in the sequel. It is also employed to a considerable extent in the same way as acetyl chloride, for determining the number of hydroxyl groups contained in carbon compounds.

Gerhardt and Laurent found that the compound $C_6H_5.CHO + C_6H_5.COCl$ is formed by the action of chlorine on benzaldehyde; this substance is insoluble in cold alcohol, crystallizes in lustrous plates, is decomposed by distillation into its components, and by boiling with water into hydrochloric acid and benzaldehydobenzoic acid;[1] the latter compound corresponds to the ethidenechloracetin (Part II. p. 72) obtained in a similar manner from acetaldehyde, and is, therefore, *benzidene benzochlorohydrin*:



$$C_6H_5.CH\begin{cases}Cl\\OCO.C_6H_5.\end{cases}$$

Benzoyl bromide, $C_6H_5.COBr$. Wöhler and Liebig, by the action of bromine on oil of bitter almonds, obtained a crystalline compound which they looked upon as benzoyl bromide. This substance was subsequently shown by Claisen to be benzidenebenzobromohydrin; this chemist then prepared benzoyl bromide by heating three molecules of benzoic acid with two molecules of phosphorus tribromide; it is a transparent, colourless liquid, has an odour resembling that of the chloride, but fumes more strongly in the air, is more readily attacked by water and boils at 218°–219°.[2] It combines with benzaldehyde to form the compound just mentioned, *benzidene benzobromohydrin* or *bromobenzylbenzoate*, $C_6H_5.CHBr.O.CO.C_6H_5$, which crystallizes from boiling petroleum ether in short prisms or thick tablets, which melt at 69°—70° and are decomposed by distillation into their components. Paternò obtained the same compound, together with ethyl bromide, benzyl bromide and benzaldehyde, by the action of bromine on ethyl benzoate, but considered it to be benzoyl bromide.[1]

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[1] *Jahresber. Chem.* 1850, 489.

[2] *Ber. Deutsch. Chem. Ges.* xiv. 2473.

Benzoyl iodide, $C_6H_5.COI$. Wöhler and Liebig obtained this compound by heating the chloride with potassium iodide as a colourless, foliated, crystalline mass, which readily melts, a little iodine being set free, has a penetrating odour and is decomposed by water and alcohol. It has not been analyzed.

Benzoyl fluoride, $C_6H_5.COF$. Borodin prepared this compound by the distillation of the chloride with acid potassium fluoride, F_2HK, in a platinum retort. It is a heavy, oily and colourless liquid, which boils at 161·5°, has a still more powerful odour than the chloride, and is decomposed by water into benzoic and hydrofluoric acids.[2]

SULPHUR COMPOUNDS OF BENZOYL.

2103 *Thiobenzoic acid*, $C_6H_5.CO.SH$. Cloëz obtained salts of this acid by the action of benzoyl chloride on potassium sulphide and double decomposition of the potassium thiobenzoate thus formed with other metallic salts.[3] The compound which he separated from the potassium salt and looked upon as thiobenzoic acid proved to be benzoyl disulphide. The free acid is obtained by decomposing the potassium salt with dilute hydrochloric acid; a yellow liquid, smelling of sulphur compounds, separates out and soon solidifies to a crystalline mass, melting at 24°, which decomposes on distillation but is volatile with steam. It is readily oxidized to benzoyl disulphide, this action taking place even when its alcoholic solution is evaporated in the air.[4]

Potassium thiobenzoate, $C_6H_5.CO.SK$, crystallizes from alcohol in yellowish tablets or prisms, and is very readily soluble in water. The silver salt is a yellowish white, and the lead salt a white precipitate; both of these readily blacken and decompose. Copper sulphate gives a greenish yellow precipitate which after some time becomes red and then contains benzoyl disulphide: ferric chloride yields a violet-brown precipitate which becomes yellow on warming.

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[1] *Gaz. Chim. Ital.* i. 586.

[2] *Ann Chem. Pharm.* cxxvi. 60.

[3] *Ibid.* cxv. 27.

[4] Engelhardt, Latschinow and Malyschew, *Zeitschr. Chem.* 1868, 353.

Ethyl thiobenzoate, $C_6H_5.CO.SC_2H_5$, is formed by the action of benzoyl chloride on lead mercaptide, $Pb(SC_2H_5)_2$,[1] and of ethyl iodide on silver thiobenzoate. It is a yellow, repulsive smelling liquid, which boils at 242°–243° and is decomposed by saponification with caustic potash into benzoic acid and ethyl hydrosulphide, while potassium hydrosulphide yields the latter compound and thiobenzoic acid. It is oxidized by potassium permanganate and dilute sulphuric acid to benzoic acid and ethylsulphonic acid.[2]

Phenyl thiobenzoate, $C_6H_5.CO.SC_6H_5$, is obtained by heating benzoyl chloride with phenyl hydrosulphide.[3] It crystallizes from alcohol or benzene in long lustrous needles, melting at 56°.

Benzyl thiobenzoate, $C_6H_5.CO.S.CH_2.C_6H_5$, is readily soluble in alcohol and benzene, and forms lustrous, asymmetric crystals, melting at 39·5°. Its behaviour towards reagents resembles that of the ethyl ether.[4]

Benzoyl sulphide, or *Thiobenzoic anhydride*, $(C_6H_5.CO)_2S$, was obtained by Wöhler and Liebig in an impure condition by the distillation of benzoyl chloride with lead sulphide. It is prepared by treating potassium thiobenzoate with benzoyl chloride (Engelhardt, Latschinow and Malyschew). It crystallizes from ether in large prisms, which melt at 48° and decompose on distillation. When heated with ammonia it yields benzamide and thiobenzoic acid; the latter is also formed by the action of potassium hydrosulphide, while benzoic acid is obtained in addition when caustic potash is employed.

Benzoyl disulphide, $(C_6H_5.CO)_2S_2$, is formed by the oxidation of thiobenzoic acid and by heating benzoic anhydride in a stream of dry sulphuretted hydrogen.[5] It is prepared by adding a solution of iodine in potassium iodide to an aqueous solution of potassium thiobenzoate. It is only slightly soluble in alcohol and ether, and crystallizes from hot carbon disulphide in large prisms or six-sided tablets which melt at 128°, and become coloured violet-red at a slightly higher temperature.

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[1] Tütschew, *Jahresber. Chem.* 1863, 483.
[2] Beckmann, *Journ. Prakt. Chem.* [2] xvii. 463.
[3] Schiller and Otto, *Ber. Deutsch. Chem. Ges.* ix. 1635.
[4] Lüders and Otto, *ibid.* xiii. 1285.
[5] Mosling, *Ann. Chem. Pharm.* cxviii. 304.

Dithiobenzoic acid, $C_6H_5.CS.SH$, is formed in small quantity when benzoyl chloride is heated with lead sulphide. It is more easily obtained by treating benzenyl trichloride with a very dilute alcoholic solution of potassium sulphide:[1]

$$C_6H_5.CCl_3 + 2K_2S = C_6H_5.CS.SK + 3KCl.$$

Acetate of lead first precipitates lead sulphide from the solution obtained, and then the lead salt of the acid, which is finally decomposed by hydrochloric acid. It is a dark violet-red, heavy, oily liquid, which gives a carmine-coloured solution in ether, and rapidly forms a resinous mass when exposed to the air.

Lead dithiobenzoate, $(C_6H_5.CS_2)_2Pb$, is a vermilion-coloured precipitate, which crystallizes from boiling xylene in fine, red needles.

Benzoyl thiocyanate, $C_6H_5.CO.S.CN$, is obtained by the action of benzoyl chloride on lead thiocyanate in the cold. It is a yellow liquid which has a penetrating odour resembling that of bitter almonds, and can only be distilled without decomposition in a vacuum.[2] It combines with ammonia, forming benzoyl thiocarbamide, $(C_6H_5.CO)HN.CS.NH_2$, and is, therefore, probably benzoyl mustard oil, $C_6H_5.CO.N.CS$.

NITROGEN COMPOUNDS OF BENZOYL.

2104 *Benzamide*, $C_6H_5.CO.NH_2$. Wöhler and Liebig obtained this compound by the action of benzoyl chloride on ammonia, and Fehling subsequently prepared it by boiling hippuric acid with water and lead dioxide.[3] Dumas found that it is also formed when ethyl benzoate is brought into contact with aqueous ammonia, the reaction taking place more rapidly when the mixture is heated to 100.°[4] It is also formed by a similar reaction from benzoic anhydride.[5]

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[1] Engelhardt and Latschinow, *Zeitschr. Chem.* 1868, 456 ; see also Fleischer, *Ann. Chem. Pharm.* cxl. 240.

[2] Miquel, *Ann. Chim. Phys.* [5] xi. 300.

[3] Fehling, *Ann. Chem. Pharm.* xxv. 48 ; Schwarz, *ibid.* lxxv. 195.

[4] *Compt. Rend.* xxv. 734.

[5] Scheitz, Marsh and Geuther, *Zeitschr. Chem.* 1868, 302.

In order to prepare it, benzoyl chloride is triturated with solid ammonium chloride, the product washed with cold water, and crystallized from hot water or alcohol;[1] or equal molecules of benzoic acid and ammonium thiocyanate may be heated to 150°—170°, carbonyl sulphide, ammonia, sulphuretted hydrogen and carbon dioxide being evolved, while benzamide remains behind and only requires to be freed from benzoic acid by washing with ammonia.[2]

It is slightly soluble in cold, more readily in hot water, especially when it contains ammonia, and dissolves readily in both alcohol and ether. When its aqueous solution is rapidly cooled, it separates out in small plates, while on more gradual cooling it is deposited in fine needles, which gradually change into larger crystals. The latter are also obtained by allowing a mixture of ethyl benzoate and ammonia to stand, or by gradually cooling the fused compound; they consist of well-formed, monoclinic tablets,[3] melting at 128°.[4] It boils at 286°—290°, a small portion being decomposed into water and benzonitril, $C_6H_5.CN$. The latter compound may be readily prepared from it by simply heating with a dehydrating agent; Wöhler and Liebig had observed that when heated with caustic baryta, an oily, aromatic liquid having a sweet taste, was formed, and that it might also be obtained by passing the vapour of the compound through a red-hot tube. This substance was afterwards recognized as the benzonitril discovered by Fehling in the year 1844.[5]

Benzamide is not decomposed by heating with dilute alkalis; when it is boiled with strong caustic potash or hydrochloric acid it decomposes into ammonia and benzoic acid, and on boiling with phenol, ammonia and phenyl benzoate are formed.[6] When heated with ethyl nitrite to 120°, the following reaction takes place:[7]

$$C_6H_5.CO.NH_2 + NO.OC_2H_5 = C_6H_5.CO.OC_2H_5 + H_2O + N_2.$$

If its solution in aqueous ether be treated with sodium amalgam and kept neutral by the addition of hydrochloric acid, benzyl alcohol is formed.[8]

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[1] Gerhardt, *Chim. Org.* iii. 268.
[2] Kekulé, *Ber. Deutsch. Chem. Ges.* vi. 113.
[3] Klein, *Ann. Chem. Pharm.* clxvi. 184.
[4] Schiff and Tassinari, *Ber. Deutsch. Chem. Ges.* x. 1785.
[5] Wöhler, *Ann. Chem. Pharm.* cxcii. 362.
[6] Guareschi, *ibid.* clxxi. 141.
[7] Meyer and Stüber, *ibid.* clxv. 186.
[8] Guareschi, *Ber. Deutsch. Chem. Ges.* vii. 1462.

It is converted into aniline by the action of bromine in alkaline solution, just as acetamide in similar circumstances yields methylamine (p. 113).

Benzamide hydrochloride, $C_6H_5.CO.NH_2.ClH$, is formed by dissolving benzamide in hot concentrated hydrochloric acid,[1] or by passing hydrochloric acid into a mixture of equal molecules of benzonitril and water.[2] It crystallizes in long prisms, which rapidly lose acid in the air.

Mercuric benzamide, $(C_6H_5.CO.NH)_2Hg$, is prepared by dissolving mercuric oxide in a hot, aqueous solution of benzamide;[3] on cooling the liquid, a semi-solid crystalline mass is formed, which is obtained by re-crystallization from alcohol in plates melting at 222°—224°.[4]

2105 *Benzoyl derivatives of amines and amido-bases* are formed by the action of benzoyl chloride on the latter:

	Melting-point.	Boiling-point.
Dimethylbenzamide:[5]		
$C_6H_5.CO.N(CH_3)_2$, large crystals .	41°—42°	255°—257°
Diethylbenzamide:[6]		
$C_6H_5.CO.N(C_2H_5)_2$, liquid	—	280°—282°
Ethylenebenzamide:[7]		
$(C_6H_5.CO.NH)_2C_2H_4$, needles . .	249°	—

Benzanilide, or *Benzoylaniline*, $C_6H_5.N(CO.C_6H_5)H$. Gerhardt obtained this compound by the action of benzoyl chloride on aniline,[8] and Leuckart found that it is also formed when phenyl isocyanate is treated with benzene in presence of aluminium chloride.[9] It is insoluble in water and crystallizes from alcohol in nacreous plates, which melt at 160°—161°,[10] and volatilize without decomposition at a higher temperature. It is not attacked by boiling aqueous acids or alkalis, but yields aniline and benzoic acid when it is fused with caustic potash. Concentrated nitric acid converts it into the three isomeric *benzoylnitranilines*, $C_6H_4(NO_2)N(CO.C_6H_5)H$:

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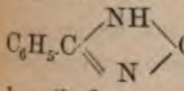
[1] Dessaignes, *Ann. Chem. Pharm.* lxxxii. 234.
[2] Pinner and Klein, *Ber. Deutsch. Chem. Ges.* x. 1896; xi. 10.
[3] Dessaignes, *loc. cit.*
[4] Oppenheim, *Ber. Deutsch. Chem. Ges.* vi. 1392.
[5] Hallmann, *ibid.* ix. 846.
[6] *Ibid.*
[7] Hofmann, *ibid.* v. 246; Kraut and Schwartz, *Ann. Chem. Pharm.* ccxxiii. 43.
[8] *Ibid.* lx. 311; lxxxvii. 164.
[9] *Ber. Deutsch. Chem. Ges.* xviii. 873.
[10] Wallach and Hofmann, *Ann. Chem. Pharm.* clxxxiv. 80.

	Melting-point.
Ortho,[1] long, light yellow needles . .	94°—95°
Meta,[2] plates	155·5°
Para,[3] small prisms	199°

The two latter are converted by reduction into the corresponding benzoyldiamidobenzenes, $C_6H_4(NH_2)N(CO.C_6H_5)H$, while the ortho-compound forms phenylenebenzamidine,



a substance which will be subsequently described.

	Melting point.
Benzoylmethylaniline :[5] $C_6H_5N(CO.C_6H_5)CH_3$, small monoclinic crystals	59°
Benzoyldiphenylamine :[6] $(C_6H_5)_2N(CO.C_6H_5)$, rhombic needles . . .	176°—177°
Benzoylorthotoluide :[7] $(C_6H_4.CH_3)N(CO.C_6H_5)H$, needles	142°—143°
Benzoylparatoluide :[8] $(C_6H_4.CH_3)N(CO.C_6H_5)H$, long needles . .	155°

2106 *Methylenedibenzamide*, $CH_2(NH.CO.C_6H_5)_2$. By heating hippuric acid, $C_9H_9NO_3$ (p. 181), with lead peroxide and dilute sulphuric or nitric acid, Schwarz obtained a crystalline substance, which he extracted from the product by alcohol. This dissolves in concentrated sulphuric or nitric acid without change, and is only attacked by oxidizing agents with difficulty and he therefore called it hipparaffin (ἵππος, parum affinis). Its analysis led to the formula $C_{16}H_{16}N_2O_2$.[9] Maier, who also prepared it, assigned to it the composition C_8H_7NO, and found that another crystalline substance, *hipparin*, $C_8H_9NO_2$, is obtained in its preparation.[10] Schwarz subsequently resumed his investigation, and showed that the latter compound is ethyl hippurate ; by heating hipparaffin with water to 170°—180°, he obtained benzamide and a substance which gave the reactions of an aldehyde, and which he identified, in spite of some differences in its properties, with the ethylenedibenzimide which he had obtained by the action of phosphorus pentoxide on a mixture of aldehyde and benzamide.[1] Kraut and Schwarz, however, found that it is actually identical with methylenedibenzamide,[2] which had been obtained by Hepp and Spiess by the action of concentrated sulphuric acid on a mixture of methylal, $CH_2(OCH_3)_2$, and benzonitril.[3]

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[1] Mears, *Ber. Deutsch. Chem. Ges.* ix. 774 ; Schwarz, *ibid.* x. 1709.

[2] Bell, *ibid.* vii. 498 ; Hübner, *ibid.* x. 1716.

[3] Stöver, *ibid.* vii. 463 and 1314.

[4] C. A. Bell, *ibid.* vii. 497 and 1504 ; Sennewald, *ibid.* ix. 775 ; Stöver, *loc. cit.*

[5] Hepp, *ibid.* x. 237.

[6] Hofmann, *Ann. Chem. Pharm.* cxxxii. 166 ; Bernthsen, *ibid.* cxcii. 13.

[7] Brückner, *ibid.* ccv. 230.

[8] Kelbe, *Ber. Deutsch. Chem. Ges.* viii. 875.

[9] *Ann. Chem. Pharm.* lxxv. 201.

[10] *Ibid.* cxxvii. 162.

It is insoluble in cold, slightly soluble in hot water, and crystallizes from alcohol in bushy aggregates of needles, melting at 223°. It is decomposed on boiling with 32 per cent. sulphuric acid, with formation of ammonia, benzoic acid and formaldehyde.

Ethidenedibenzamide, $CH_3.CH(NH.COC_6H_5)_2$. Limpricht obtained this compound by the action of benzoyl chloride on aldehyde-ammonia,[4] and Nencki by that of benzamide on aldehyde containing a few drops of hydrochloric acid.[5] It is prepared by adding first paraldehyde and then benzonitril to well-cooled sulphuric acid, and diluting with water after some hours (Hepp and Spiess). It crystallizes from alcohol in long, white needles, which melt at 204° and sublime without decomposition. It is decomposed by fuming nitric acid into aldehyde and benzamide.

Dibenzamide, $N(CO.C_6H_5)_2H$, was prepared by Baumert and Landolt, together with benzamide, by the action of benzoyl chloride on potassium amide.[6] Barth and Senhofer found that it is readily formed when benzonitril is treated with a mixture of sulphuric acid and phosphorus pentoxide; the solution is allowed to stand for some hours and then diluted with water, which slowly precipitates the compound in crystals:[7]

$$2C_6H_5.CN + 2H_2O = (C_6H_5.CO)_2NH + NH_3.$$

It is also formed when lophine, which is obtained by the dry distillation of hydrobenzamide, is treated with a solution of chromium trioxide in acetic acid, it being thus smoothly converted into benzamide and dibenzamide:[8]

$$C_{21}H_{16}N_2 + 2O + H_2O = C_7H_5O.NH_2 + (C_7H_5O)_2NH.$$

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[1] *Wien. Akad. Ber.* lxxvii. 762.

[2] *Ann. Chem. Pharm.* ccxxiii. 40.

[3] *Ber. Deutsch. Chem. Ges.* ix. 1424.

[4] *Ann. Chem. Pharm.* xcix. 119.

[5] *Ber. Deutsch. Chem. Ges.* vii. 159.

[6] *Ann. Chem. Pharm.* cxi. 5.

[7] *Ber. Deutsch. Chem. Ges.* ix. 975, 1073.

[8] E. Fischer and Proschke, *ibid.* xiii. 708.

It separates from dilute alcohol in long, thin needles, which melt at 148°, and decompose at a higher temperature, giving off an odour of benzaldehyde. It is almost insoluble in cold and scarcely soluble in hot water, but dissolves readily in ether, chloroform and benzene, from the last two of which it separates in rhombic crystals. On boiling with caustic potash it decomposes into benzoic acid and ammonia.

It dissolves readily in dilute caustic soda, the solution when concentrated depositing small glittering needles of the compound $(C_7H_5O)_2NNa$; it also occurs in short, distorted prisms containing half a molecule of water, which is lost at 120°. The solution gives a precipitate with silver nitrate, consisting of $(C_7H_5O)_2NAg$, and is also precipitated by other metallic salts.

Schäfer, by heating benzamide in a stream of hydrochloric acid, obtained a compound which he considered to be *dibenzamide hydrate* $(C_7H_5O)_2NH+2H_2O$; it crystallizes in small plates, which melt at 99°, and do not lose water at a higher temperature, but decompose into benzoic acid and benzamide.[1] This substance is evidently acid ammonium benzoate, $C_7H_5(NH_4)O_2+C_7H_6O_2$.[2]

Dibenzanilide, $(C_6H_5.CO)_2NC_6H_5$. Gerhardt and Chiozza obtained this compound by the action of benzoyl chloride on benzanilide. It crystallizes from alcohol in fine, lustrous needles, which melt at 137° and sublime when more strongly heated.[3] By heating benzoic acid with phenyl mustard oil, Losanitsch obtained a crystalline, foliaceous mass of a dibenzanilide, melting at 155°.[4] Steiner, on the other hand, who prepared it by Gerhardt's method and also by heating tribenzhydroxylamine, $N(OC_7H_5O)(C_7H_5O)_2$, found the melting-point of both preparations to be 161°.[5]

Thiobenzamide, $C_6H_5.CS.NH_2$, was prepared by Cahours by passing sulphuretted hydrogen into an alcoholic, ammoniacal solution of benzonitril:

$$C_6H_5.CN+SH_2=C_6H_5.CS.NH_2.$$

It crystallizes from hot water in long, yellow needles, melting at 117°; when heated with water and mercuric oxide, it is reconverted into benzonitril, while it is reduced to benzylamine by zinc and hydrochloric acid.[1] Iodine acts upon its alcoholic solution in the following manner:

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[1] *Ann. Chem. Pharm.* clxix. 111.
[2] Beilstein, *Org. Chem.* 1101.
[3] *Ann. Chem. Pharm.* lxxxvii. 302.
[4] *Ber. Deutsch. Chem. Ges.* vi. 176.
[5] *Ann. Chem. Pharm.* clxxviii. 235.

$$2C_7H_7SN + 2I_2 = C_{14}H_{10}SN_2 + 4HI + S.$$

The compound obtained in this way crystallizes from hot alcohol in lustrous, snow-white needles, which melt at 90° and distil without decomposition at a higher temperature. It is a very stable compound, and is not altered by being heated to 150° with hydrochloric acid, sulphuric acid or tolerably concentrated nitric acid. On boiling with caustic potash it is gradually converted into benzoic acid, ammonia being evolved. Zinc and hydrochloric acid reduce it in alcoholic solution to the base, $C_{14}H_{14}N_2$,[2] which is isomeric with ethenyldiphenylamidine (Part III. p. 217); benzene and benzonitril are simultaneously formed.[3] It crystallizes in small plates, melting at 71°, is a monacid base and forms an alkaline solution in alcohol.

Thiobenzanilide, or *Phenylthiobenzamide*, $C_6H_5.CS.N(C_6H_5)H$, is formed when benzanilide is heated with phosphorus pentasulphide,[4] and crystallizes from alcohol in thin, yellow tablets or prisms, melting at 97·5°—98·5°.

Diphenylthiobenzamide, $C_6H_5.CS.N(C_6H_5)_2$, is formed when asymmetric diphenylbenzenylamidine is heated to 130°—140° with carbon disulphide:

$$C_6H_5.C(NH)N(C_6H_5)_2 + CS_2 = C_6H_5.CS.N(C_6H_5)_2 + CNSH.$$

It crystallizes from solution in benzene or alcohol in dark yellow, asymmetric prisms, melting at 150°—151°.[5]

2107 *Benzoyl urea*, $C_6H_5.CO.NH.CO.NH_2$. Zinin obtained this compound by heating urea to 150°—155° with benzoyl chloride;[6] the anhydride may be substituted for the chloride in this reaction.[7] The monobenzoyl urea crystallizes from alcohol in long, thin plates, which melt at about 200° and decompose into benzamide and cyanuric acid when carefully heated beyond this point.

Symmetric ethylbenzoyl urea,[8] $CO\left\{\begin{array}{l}NH.C_2H_5\\NH.CO.C_6H_5\end{array}\right.$, needles.

Asymmetric ethylbenzoyl urea,[9] $OC\left\{\begin{array}{l}NH_2\\N(C_2H_5)CO.C_6H_5\end{array}\right.$, rhombohedra.

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[1] Hofmann, *Ber. Deutsch. Chem. Ges.* i. 102.

[2] *Ibid.* ii. 644.

[3] Wanstrat, *ibid.* vi. 335.

[4] Bernthsen, *ibid.* xi. 503.

[5] Bernthsen, *Ann. Chem. Pharm.* cxcii. 37.

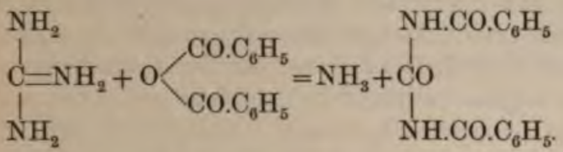
[6] *Ibid.* xcii. 404.

[7] Geuther, Scheitz and Marsh, *Zeitschr. Chem.* 1868, 305.

[8] Leuckart, *Journ. Prakt. Chem.* [2] xxi. 33; Miquel, *Ann. Chim. Phys.* [5] xi. 318.

[9] Lössner, *Journ. Prakt. Chem.* [2] x. 251.

Dibenzoyl urea, $CO(NH.CO.C_6H_5)_2$, is formed, together with hydrochloric acid, carbon dioxide, ammonium chloride, benzoic acid and benzonitril, when benzamide is heated to 160°—170° with carbonyl chloride,[1] and also from guanidine and benzoic anhydride at 100°:[2]



$$\begin{array}{c}NH_2\\ |\\ C{=}NH_2\\ |\\ NH_2\end{array} + O\begin{array}{l}\diagup CO.C_6H_5\\ \diagdown CO.C_6H_5\end{array} = NH_3 + \begin{array}{c}NH.CO.C_6H_5\\ |\\ CO\\ |\\ NH.CO.C_6H_5.\end{array}$$

It crystallizes from alcohol in needles melting at 210°, and is decomposed by boiling with strong acids into carbon dioxide, ammonia and benzoic acid, while dilute caustic potash solution converts it into benzamide and carbon dioxide.

Benzoyl thio-urea, $C_6H_5.CO.NH.CS.NH_2$, is formed when thio-urea is heated with benzoyl chloride[3] and by the action of dilute ammonia on benzoyl thiocyanate.[4] It crystallizes from dilute alcohol in small prisms which have a very bitter taste and melt at 171°.

Miquel has prepared the following compounds by the action of benzoyl thiocyanate on amines and amido-bases:

	Melting-point.
Ethylbenzoyl thio-urea:	
$CS\left\{\begin{array}{l}NH.CO.C_6H_5\\ NH.C_2H_5\end{array}\right.$, fine prisms. . . .	134°
Phenylbenzoyl thio-urea:	
$CS\left\{\begin{array}{l}NH.CO.C_6H_5\\ NH.C_6H_5\end{array}\right.$, long needles. . . .	148°—149°
Benzylbenzoyl thio-urea:	
$CS\left\{\begin{array}{l}NH.CO.C_6H_5\\ NH.CH_2.C_6H_5\end{array}\right.$, small prisms. . .	145°
Paratolylbenzoyl thio-urea:	
$CS\left\{\begin{array}{l}NH.CO.C_6H_5\\ NH.C_6H_4.CH_3\end{array}\right.$, long prisms. . . .	165°

Benzoylphenylhydrazine, $C_6H_5.NH-NH(CO.C_6H_5)$. In order to obtain this compound, two molecules of phenylhydrazine are dissolved in five times their amount of ether, the solution cooled assumed that hippuric acid is a copulated compound of benzoic acid and glycocoll, although as was pointed out by Berzelius, this assumption does not in the least account for the action of lead dioxide.

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[1] Schmidt, *Journ. Prakt. Chem.* [2] v. 58.
[2] Creath, *Ber. Deutsch. Chem. Ges.* vii. 1739.
[3] Pike, *ibid.* vi. 755.
[4] Miquel, *Ann. Chim. Phys.* [5] xi. 313.

An important advance towards the determination of the constitution of hippuric acid was made by Strecker,[1] who found that it is converted by the action of nitrous acid into benzoylglycollic acid (p. [illegible]), which was more closely investigated by him in conjunction with Socoloff. This compound assumes the elements of water and splits up into benzoic acid and glycollic acid, and must, therefore, be considered as a copulated compound of these, its amido-derivative being hippuric acid.[2]

Dessaignes now endeavoured to prepare hippuric acid artificially by heating glycocoll with benzoyl chloride, but without success. He attributed his failure to the evolution of hydrochloric acid and therefore substituted the zinc salt of glycocoll, zinc amido-acetate, and found that hippuric acid is slowly formed when benzoyl chloride is allowed to act upon this in the cold, more rapidly at 120°.[3] He also obtained it subsequently by heating benzoic acid with glycocoll to 160°,[4] and Jazukowitzsch prepared it by heating chloracetic acid with benzamide;[5] the yield was, however, small owing to the formation of free hydrochloric acid. These syntheses finally proved that hippuric acid is benzoylamido-acetic acid:

$$\begin{array}{l} CH_2.NH_2 \\ COOH \end{array} + HO.CO.C_6H_5 = \begin{array}{l} CH_2.NH.CO.C_6H_5 \\ \vert \\ CO.OH \end{array} + H_2O.$$

$$\begin{array}{l} CH_2Cl \\ \vert \\ CO.OH \end{array} + NH_2.CO.C_6H_5 = \begin{array}{l} CH_2.NH.CO.C_6H_5 \\ \vert \\ CO.OH \end{array} + HCl.$$

It is also formed, together with other products which will be subsequently mentioned, from benzoyl chloride and silver amidoacetate,[6] and very readily when glycocoll is heated with benzoic anhydride [7] or when benzoyl chloride is added to a concentrated aqueous solution of the former.[8]

Liebig detected it in human urine, about 1 grm. being excreted per diem.[1] According to Weismann it is formed more freely during a vegetable than an animal diet,[2] and according to Ducheck it is not invariably present.[3] Pettenkofer found 1·3 per cent. of it in the urine of a girl suffering from St. Vitus's dance, whose diet consisted exclusively of apples and bread; the amount decreased as soon as meat was again taken.[4]

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[1] *Ann. Chem. Pharm.* lxviii. 54.

[2] *Ibid.* lxxx. 17.

[3] *Ibid.* lxxxvii. 325.

[4] *Jahresber. Chem.* 1857, 367.

[5] *Zeitschr. Chem.* 1867, 466.

[6] *Journ. Prakt. Chem.* [2] xxiv. 239 ; xxvi. 145.

[7] Curtius, *Ber. Deutsch. Chem. Ges.* xvii. 1662.

[8] Baum, *Zeitschr. Physiolog. Chem.* ix. 465.

Lehmann observed its occurrence during diabetes, even before Liebig had detected its presence in normal human urine,[5] and since that time it has frequently been observed in large quantities in diabetic urine. It also occurs largely in the acid urine of persons suffering from fevers of every kind.[6]

Liebig,[7] and Dumas[8] assumed that fresh horses' urine contains hippuric acid which is converted into benzoic acid on standing. The former subsequently stated that horses and bullocks excrete hippuric acid when they are allowed to remain idle for some time, and benzoic acid when they are working to the full extent of their powers,[9] and Erdmann and Marchand found[10] that the urine of carriage horses usually contains the former and that of plough horses the latter. Lehmann, however, who investigated the urine of a large number of horses, both sound and diseased, well and badly fed, found only hippuric acid without exception, provided that the urine had not been allowed to stand too long in the air. After standing for a considerable time, and especially after the formation of ammonia, only benzoic acid is present, being formed by a special ferment. When such urine was added to a sample of the fresh material, containing hippuric acid alone, the latter decomposed on evaporation and only benzoic acid could then be detected.[11] Roussin found a large quantity of urea but no hippuric acid in the urine of Arab stallions, which did not work but were kept for breeding; that of others, which were used by the Spahis for riding, contained little urea, but 0·5—1 per cent. of hippuric acid; in one sample of urine which was passed after a long journey the amount rose to 1·4 per cent., and 0·78 per cent. was found in that of omnibus horses.[12]

Städeler found about 1·5 per cent. of hippuric acid in cows' urine,[1] and, according to Hallwachs, a cow passes more than 50 grms. of the acid during twenty-four hours.[2] Kraut observed that cows which are allowed to graze give more hippuric acid than those which are stall fed,[3] while only traces are formed when they are fed on spent grain from a distillery.[4]

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[1] Baum, *Zeitschr. Physiolog. Chem.* cvi. 164.

[2] *Jahresber. Chem.* 1858, 572.

[3] Gmelin, *Org. Chem.* v. 332.

[4] *Ann. Chem. Pharm.* lii. 86.

[5] *Journ. Prakt. Chem.* vi. 113.

[6] Gmelin's *Org. Chem.* v. 334.

[7] *Ann. Chem. Pharm.* xxx. 280.

[8] *Ann. Chim. Phys.* lvii. 331.

[9] *Ann. Chem. Pharm.* xli. 272; *Organ. Chem. in Anwendung auf Phys. und Pathol.* lxxxiv.

[10] *Journ. Prakt. Chem.* xxvi. 491.

[11] Gmelin, *Organ. Chem.* v. 332.

[12] *Compt. rend.* xlii. 583.

In the urine of cows fed on oat-straw and wheat-straw, with the addition of some beans, 2·1—2·7 per cent. was found, while that of cattle fed on bean-straw and clover contained only 0·4 per cent., and when ordinary meadow hay was given, 1·4 per cent.[5] The urine of sucking calves contains uric acid but no hippuric acid (Wöhler). The latter occurs in the urine of sheep, goats, hares, rabbits, and elephants (Schwarz). Schwarz found it in very considerable quantity in the urine of a camel, the sample being very concentrated, as only four ounces were passed during the day, and Lehmann detected it in the urine of the tortoise (*Testudo graeca*). Pettenkofer observed its occurrence in the scurf which is formed on the skin during the rare disease known as ichthiosis,[6] and J. Davy found it in butterflies, moths, and their chrysalides and excrements.[7]

The urine of dogs also contains a small quantity of the acid even during an exclusively meat diet or after long fasting,[8] while it has never been found in the urine of pigs.[9]

2109 Ure was the first to make the important observation that the urine of a patient who has taken benzoic acid contains a large amount of hippuric acid.[10] Wöhler had previously suggested that benzoic acid is changed to hippuric acid in the organism, for he had found in the urine of a dog to which half a drachm of benzoic acid had been given an acid which he mistook for benzoic acid, but which he subsequently found to be identical with the hippuric acid discovered by Liebig.[11] Under his directions Keller conducted a research on the subject, taking 2 grains of benzoic acid in the evening and repeating the dose three times daily during the following days. His urine, which now possessed a strongly acid reaction, contained a considerable amount of hippuric acid, and, as Wöhler says, "since benzoic acid seems not to affect the health, large quantities of hippuric acid might readily be prepared in this manner, the only requisite being a man who would continue the manufacture for weeks.[1] These observations were confirmed by Garrod,[2] Schwarz and others; Marchand found 39·2 grains of hippuric acid in his urine after eating 30 grains of benzoic acid.[3]

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[1] *Ann. Chem. Pharm.* lxxvii. 17.

[2] *Ibid.* cv. 209.

[3] *Chem. Centralbl.* 1858, 831.

[4] Schwarz, *Ann. Chem. Pharm.* liv. 31.

[5] Henneberg, Stohmann and Rautenberg, *ibid.* cxxiv. 201.

[6] *Ibid.* xc. 378.

[7] *New Edinb. Phil. Journ.* xlv. 17.

[8] Salkowski, *Ber. Deutsch. Chem. Ges.* xi. 500.

[9] Boussingault, *Ann. Chim. Phys.* [3] xv. 97; von Bibra, *Ann. Chem. Pharm.* liii. 98.

[10] *Repert. Pharm.* xxvii. 642.

[11] Berzelius, *Lehrb. Chem.* 1831, iv. 376.

Many other compounds, which are converted into benzoic acid by oxidation, are changed into hippuric acid by their passage through the organism; such are benzaldehyde,[4] cinnamic acid,[5] $C_6H_5.CH{=}CH.CO_2H$, hydrocinnamic acid or phenylpropionic acid,[6] $C_6H_5.C_2H_4.CO_2H$, phenylglycollic acid,[7] $C_6H_5.CH(OH)CO_2H$, quinic acid,[8] $C_6H_7(OH)_4CO_2H$, and even toluene.[9] The substitution products of benzoic acid appear in the urine as the corresponding derivatives of hippuric acid; thus phenylacetic acid, $C_6H_5.CH_2.CO_2H$, gives phenylaceturic acid[10]; salicylic acid, $C_6H_4(OH)CO_2H$, is converted into salicyluric acid,[11] and toluic acid, $C_6H_4(CH_3)CO_2H$, into toluyluric acid;[12] phthalic acid, however, remains unchanged.[13] It follows from this, that the monobasic aromatic acids, and hydroxy-acids, combine with glycocoll with elimination of water in their passage through the organism.

After Liebig had discovered hippuric acid, he raised the question whether it must be considered as a compound of benzoic acid with an unknown compound body, or as a peculiar acid by the decomposition of which benzoic acid is formed, just as oxalic and formic acids are formed when sugar or starch is treated with nitric acid. He decided for the latter view, and says: "The first view is rendered improbable by the fact that I have been unable to prepare even the slightest trace of benzoic acid from horses' fodder, which is the source of their urine, even if this acid be contained in *Anthoxanthum odoratum* and *Holcus odoratus*, as found by Vogel, its identity being rendered doubtful by its different crystalline form." These fragrant grasses were afterwards found to contain not benzoic acid but coumarin, $C_9H_6O_2$, which is the anhydride of orthohydroxyphenylacrylic acid, $C_6H_4(OH)C_2H_2.CO_2H$.

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[1] *Ann. Chem. Pharm.* xliii. 108.
[2] *Phil. Mag.* xx. 501.
[3] *Journ. Prakt. Chem.* xxxv. 309.
[4] Frerichs and Wöhler, *Ann. Chem. Pharm.* lxviii. 336.
[5] Erdmann and Marchand, *Journ. Prakt. Chem.* xxvi. 491.
[6] E. and H. Salkowski, *Ber. Deutsch. Chem. Ges.* xii. 653.
[7] Gräbe and Schultzen, *Ann. Chem. Pharm.* cxlii. 349.
[8] Lautemann, *ibid.* cxxv. 12.
[9] Nauyen and Schultzen, *Zeitschr. Chem.* 1868, 29.
[10] E. and H. Salkowski, *loc. cit.*
[11] Bertagnini, *Ann. Chem. Pharm.* xcvii. 249.
[12] Kraut, *ibid.* xcviii. 360.
[13] Gräbe and Schultzen, *loc. cit.*

After it had been proved that benzoic acid and allied substances are converted into hippuric acid in the organism, it seemed probable that that occurring in the urine of graminivora would be derived from benzoic acid or other benzoyl compounds occurring in the fodder. Hallwachs, therefore, investigated the chief grasses and plants in question, but was unable to detect the slightest trace of benzoic acid or any other compound which could yield hippuric acid; he also showed that coumarin and chlorophyll, which might be looked upon as allies of the benzoyl series, pass through the organism unchanged.[1]

O. Loew found, however, that quinic acid, which occurs in many plants, is also present in hay, and considered it to be the source of the hippuric acid.[2] Although the latter acid can be obtained from quinic acid, it passes through the organism almost unchanged, only a very small portion being converted into hippuric acid.[3]

The amount of hippuric acid in the urine is naturally greater when such fruits as plums and cranberries, which contain benzoic acid, have been eaten;[4] but Ducheck found a much larger quantity than would correspond to the amount of benzoic acid contained in the plums.

As already mentioned, hippuric acid occurs largely in the urine of diabetic patients who subsist on a meat diet, and in that of others who have passed several days without taking food, as well as in small quantity in the urine of dogs after a meat diet or long fasting.

It follows from these facts with tolerable certainty that the hippuric acid, or rather the aromatic group contained in it, is derived from the albuminoids, which are known to yield benzaldehyde and benzoic acid on oxidation, while phenylpropionic acid is formed from them by the pancreatic fermentation (E. and H. Salkowski).

E. Salkowski has adduced a further proof for this in the fact that phenylaceturic acid, $(C_6H_5.CH_2.CO)NH.CH_2.CO_2H$, which is the homologue of hippuric acid, occurs in horses' urine and can readily be split up into glycocoll and phenylacetic acid, $C_6H_5.CH_2.CO_2H$. The latter acid is also formed, together with phenylpropionic acid, by the putrefraction of albumen.[1]

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[1] *Ann. Chem. Pharm.* cv. 207.

[2] *Journ. Prakt. Chem.* [2] xix. 309.

[3] Stadelmann, *Jahresber. Chem.* 1879, 982.

[4] Ducheck, *Gmelin's Org. Chem.* v. 332; Thudichum, *Jahresber. Chem.* 1863, 656.

The source of the hippuric acid is therefore identical with that of the uric acid, which is especially formed in the organism of the carnivora.

2110 The acid is best prepared from the urine of cows or oxen, which often contains such a large quantity that it is precipitated by the addition of hydrochloric acid. If this be not the case, the urine is boiled up with milk of lime, filtered, and the filtrate neutralized with hydrochloric acid, evaporated, and then treated with an excess of hydrochloric acid.[2] Putz proposes to precipitate the neutral solution with ferric chloride and decompose the washed precipitate with hydrochloric acid.[3] The acid obtained by these methods is always discoloured, but the impurity may be removed by dissolving it in warm chlorine water,[4] or treating its aqueous solution with bleaching powder.[5] It is more convenient to effect the purification by allowing 3 parts of the acid to stand in contact with 1 part of nitric acid, of sp. gr. 1·3, and filtering off the mother-liquor after twenty-four hours.[6] It can also be dissolved in hot, dilute caustic soda solution and treated with potassium permanganate until yellow crystals separate out on the addition of hydrochloric acid.[7] These are boiled with water and animal charcoal and then finally re-crystallized from hot water.

Hippuric acid is also readily obtained when finely powdered, dry amido-acetic acid is gradually added to an excess of heated benzoic anhydride, and the mixture heated on an oil-bath until it becomes coloured red. It is then allowed to cool, dissolved in water and neutralized with caustic soda, the solution being subsequently acidified with hydrochloric acid and allowed to stand for several days. The precipitated hippuric acid is boiled with water and animal charcoal, the filtrate concentrated on the water-bath and then allowed to cool slowly. The large crystals which are formed are then washed with petroleum spirit to remove any adhering benzoic acid.[8]

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[1] *Ber. Deutsch. Chem. Ges.* xvii. 3010.
[2] Gregory, *Ann. Chem. Pharm.* lxiii. 125.
[3] *Jahresber. Chem.* 1877, 795.
[4] Dauber, *Ann. Chem. Pharm.* lxxiv. 202.
[5] Conrad, *Journ. Prakt. Chem.* [2] xv. 244.
[6] Hutstein, *Jahresb.* 1854, 453.
[7] Gössmann, *Ann. Chem. Pharm.* xcix. 374 ; Conrad, *loc. cit.*
[8] Curtius, *Ber. Deutsch. Chem. Ges.* xvii. 1662.

Properties.—It forms long, lustrous, rhombic prisms or needles (Fig. 1), which are sometimes opaque, and which dissolve in 600 parts of water at 0°; it is only slightly soluble in cold alcohol and ether, but dissolves readily in warm water and alcohol. It is insoluble in petroleum spirit, and can be separated from benzoic acid by means of this property. It reddens litmus, but has not a sour taste, melts at 187·5° (Conrad) and decomposes at temperatures above 240°, with formation of hydrocyanic acid, benzoic acid, benzonitril, and a black, resinous substance.[1] When it is heated with caustic potash to 260°, ammonia and benzonitril are given off, while calcium carbonate, calcium benzoate and carbon remain behind. Caustic baryta effects a similar decomposition, barium cyanate being formed in addition, while when an excess of baryta is employed, benzene, ammonia and methylamine are given off and barium carbonate and benzoate formed, but no cyanide.[2] It has been already mentioned that on heating with strong acids or alkalis it decomposes into benzoic acid and glycocoll; these products are also formed when it is heated to 120° with a concentrated solution of zinc chloride; when, however, it is distilled with anhydrous zinc chloride, benzonitril and carbon dioxide are formed.[3]

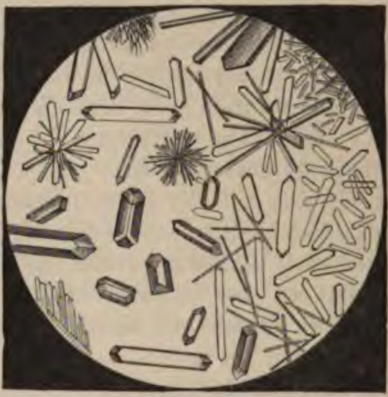

FIG. 1.

On oxidation with lead dioxide and sulphuric acid or with nitric acid, it is converted into hipparaffin or methylenedibenzamide (p. 175):

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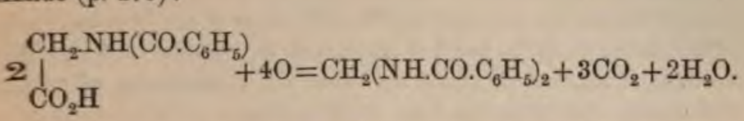
[1] Limpricht and Uslar, *Ann. Chem. Pharm.* lxxxviii. 133.
[2] Kraut, *Jahresber.* 1863, 348; Conrad, *loc. cit.*
[3] Gössmann, *Ann. Chem. Pharm.* c. 69.



$$2\begin{array}{l}CH_2.NH(CO.C_6H_5)\\ \vert\\ CO_2H\end{array}+4O=CH_2(NH.CO.C_6H_5)_2+3CO_2+2H_2O.$$

The substitution products of hippuric acid will be described among the corresponding derivatives of benzoic acid.

2111 *The Hippurates.* Hippuric acid decomposes carbonates and dissolves zinc with evolution of hydrogen. Its salts are for the most part soluble in water and crystallize well; they have been investigated by Schwarz.[1]

Potassium hippurate, $C_9H_8KNO_3+H_2O$, forms vermicular crusts consisting of pointed rhombic prisms; on heating it forms a vapour which possesses a smell resembling that of *Satureja hortensis.* It combines with hippuric acid forming the acid salt, $C_9H_8KNO_3+C_9H_9NO_3+H_2O$, which crystallizes in quadratic tablets possessing a satin lustre.

Sodium hippurate, $4C_9H_8NaNO_3+H_2O$, is a crystalline mass which readily dissolves in water and hot alcohol.

Acid ammonium hippurate, $C_9H_8(NH_4)NO_3+C_9H_9NO_3+H_2O$, crystallizes in small, quadratic prisms; the normal salt has not been prepared.

Calcium hippurate, $(C_9H_8NO_3)_2Ca+3H_2O$, forms rhombic prisms,[2] which are soluble in 18 parts of cold and 6 parts of boiling water (Liebig).

Strontium hippurate, $(C_9H_8NO_3)_2Sr+5H_2O$, crystallizes in fascicular aggregates, composed of four-sided prisms; it is only slightly soluble in cold water and alcohol, but dissolves readily in them when hot.

Barium hippurate, $(C_9H_8NO_3)_2Ba+H_2O$, crystallizes in crusts made up of quadratic prisms. Schwarz, in endeavouring to separate a mixture of hippuric and benzoic acids by means of their barium salts, obtained, first, barium benzoate, then barium hippurate, and, finally, from the mother-liquor, the double salt, $C_7H_5O_2.Ba.C_9H_8NO_3+5H_2O$, in characteristic warty masses.[3]

Magnesium hippurate, $(C_9H_8NO_3)_2Mg+5H_2O$, forms warty crystals.

Zinc hippurate, $(C_9H_8NO_3)_2Zn+5H_2O$, crystallizes in small plates, which after dehydration dissolve in 532 parts of water at 17° and in 4 parts at 100°.

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[1] *Ann. Chem. Pharm.* liv. 33.
[2] Schabus, *Jahresber. Chem.* 1850, 411.
[3] *Ann. Chem. Pharm.* lxxv. 192.

Lead hippurate, $(C_9H_8NO_3)_2Pb + 2H_2O$, is a curdy precipitate crystallizing from a large quantity of hot water in fine, silky needles, which then suddenly take up a molecule of water and change into lustrous four-sided tablets.

Copper hippurate, $(C_9H_8NO_3)_2Cu + 3H_2O$, is slightly soluble in cold water, more readily in hot alcohol, and crystallizes in small, pointed, rhombic prisms of a blue colour.

Silver hippurate, $2C_9H_8AgNO_3 + H_2O$, is a curdy precipitate, which crystallizes from hot water in aggregates of lustrous needles.

When ferric chloride is added to a solution of a normal hippurate, a cream-coloured precipitate of ferric hippurate is thrown down, which contains more or less basic salt according to the greater or less dilution of the solution; this fact was discovered by [illegible] who employed the compound for the preparation of hippuric acid from urine. It is almost insoluble in pure water, but dissolves in presence of free hippuric acid, an excess of ferric chloride and in alcohol. Wreden has proposed to employ this reaction for the determination of hippuric acid in urine. Henneberg, Stohmann and Rautenberg, found that it is most convenient for this purpose to make use of a solution of ferric nitrate which has been standardized with pure hippuric acid. The urine is acidified with nitric acid, heated to boiling to remove carbon dioxide, neutralized with calcium carbonate, treated with an excess of lead nitrate, and then diluted to a known volume and filtered. An aliquot portion of the filtrate is heated and titrated with the ferric nitrate solution until a drop of the clear liquid gives a blue colouration with potassium ferrocyanide, the distinction between this and the white of the lead ferrocyanide which is formed at first, being very sharp.[2]

Methyl hippurate, $C_9H_8(CH_3)NO_3$, is obtained by the action of hydrochloric acid on a hot solution of hippuric acid in methyl alcohol.[3] It is slightly soluble in cold, more readily in hot water and in alcohol, and crystallizes in long, white prisms, which melt at 80·5°, and decompose at 250° with formation of ammonia and benzonitril.

Ethyl hippurate, $C_9H_8(C_2H_5)NO_3$, is formed in a similar

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[1] Löwe, *Jahresber.* 1855, 536.

[2] *Ann. Chem. Pharm.* cxxiv. 182.

[3] Jaquemin and Schlagdenhauffen, *Compt. Rend.* xlv. 1011; Conrad, *Journ. Prakt. Chem.* [2] xv. 247.

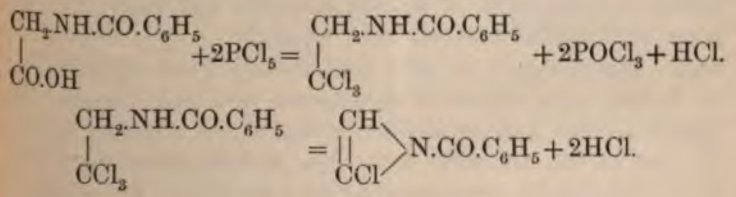
manner to the methyl ether,[1] and also by allowing a saturated, warm alcoholic solution of hippuric acid to stand for a month in a warm place.[2]

It may also be readily prepared by heating ethyl amido-acetate with benzoic anhydride to 100°.[3] It crystallizes from hot water in long, white, silky needles, which melt at 60·5°, have no odour, but a sharp taste resembling that of oil of turpentine, and decompose on heating. On distillation with steam, it decomposes into alcohol and the free acid.

The following ethers have also been prepared :[4]

	Melting-point.
Butyl hippurate, $C_9H_8(C_4H_9)NO_3$, prisms	40°—41°
Isobutyl hippurate, $C_9H_8(C_4H_9)NO_3$ small, rhombic prisms	45°—46°
Amyl hippurate, $C_9H_8(C_5H_{11})NO_3$, small needles	27°—28°

When hippuric acid is distilled with phosphorus pentachloride, hydrochloric acid is evolved and the distillate consists, first, of phosphorus oxychloride, then of benzoyl chloride and finally of the compound C_9H_6ClNO, which crystallizes from ether in flat, four-sided, monoclinic prisms, melting at 40°—50°. It boils at 220°, is not attacked by alcoholic potash, and on fusion with potash yields benzoic acid and ammonia.[5] The formation of this substance may be explained by the following equations:



$$\begin{array}{l}CH_2.NH.CO.C_6H_5\\ |\\ CO.OH\end{array} + 2PCl_5 = \begin{array}{l}CH_2.NH.CO.C_6H_5\\ |\\ CCl_3\end{array} + 2POCl_3 + HCl.$$

$$\begin{array}{l}CH_2.NH.CO.C_6H_5\\ |\\ CCl_3\end{array} = \begin{array}{l}CH\\ \|\\ CCl\end{array}\!\!>N.CO.C_6H_5 + 2HCl.$$

Hippuramide, $(C_6H_5.CO)NH.C_2H_2O.NH_2$, is formed by the action of aqueous ammonia on the ethyl ether; it separates from hot water in short, thick crystals, melting at 183° (Jaquemin and Schlagdenhauffen ; Conrad).

Hippuramido-acetic acid, $C_{11}H_{12}N_2O_4$, is formed, together with hippuric acid, by the action of benzoyl chloride on silver amido-acetate, and is probably derived from the hippuric acid which is first formed:

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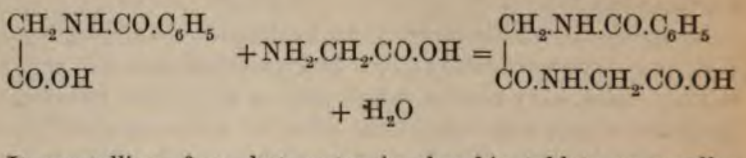
[1] Stenhouse, *Ann. Chem. Pharm.* ; xxi. 148 ; Conrad, *loc. cit.*

[2] Liebig, *Ann. Chem. Pharm.* lxv. 351.

[3] Curtius, *Ber. Deutsch. Chem. Ges.* xvii. 1662.

[4] Campani and Bizzarri, *Bull. Soc. Chim.* xxxv. 427 ; Campani, *Ber. Deutsch. Chem. Ges.* xi. 1247.

[5] Schwanert, *Ann. Chem. Pharm.* cxii. 59.



$$\begin{array}{l} CH_2.NH.CO.C_6H_5 \\ | \\ CO.OH \end{array} + NH_2.CH_2.CO.OH = \begin{array}{l} CH_2.NH.CO.C_6H_5 \\ | \\ CO.NH.CH_2.CO.OH \end{array} + H_2O$$

It crystallizes from hot water in rhombic tablets or needles, melting at 206·5°. On boiling with hydrochloric acid, it decomposes into amido-acetic acid and benzoic acid; on heating with dilute acids, on the other hand, both hippuric acid and amido-acetic acid are formed. Its salts crystallize well; the ethyl ether, which melts at 117°, combines with ammonia forming *hippurglycollamide*, which crystallizes in large, transparent plates, melting at 202°.

An acid, $C_{10}H_{12}N_3O_4$, is also formed by the reaction just mentioned, and crystallizes from hot water in microscopic needles which melt at 240°, and are decomposed by hot hydrochloric acid into amido-acetic acid, benzoic acid, and a non-crystallizable, nitrogenous compound.[1]

Hydrobenzuric acid, $C_{18}H_{24}N_2O_6$, is obtained by the action of sodium amalgam on a concentrated solution of hippuric acid in caustic soda solution; it forms a mass resembling turpentine, and becomes crystalline after standing for months. When it is treated with an excess of sodium amalgam and water, it decomposes into *hydrobenzyluric acid*, $C_{16}H_{21}NO_4$, and amido-acetic acid. The former is an oily liquid, which gradually solidifies; on boiling with alkalis it decomposes into hydrobenzoic acid, benzyl alcohol and amido-acetic acid. Its alkaline solution oxidizes in the air with formation of *hydroxybenzyluric acid*, $C_{16}H_{21}NO_5$, which is a crystalline mass melting at 60°—70°.[2]

2112 *Ornithuric acid*, $C_{19}H_{20}N_2O_4$. Shepard found that benzoic acid is not converted into hippuric acid in the organism of birds, but into another nitrogenous compound, which was more closely examined by Jaffé.[3] He obtained it from the excrements of hens which were fed with benzoic acid; it is very slightly soluble in water and crystallizes from hot alcohol in minute needles, melting at 182°. Its solution reddens litmus. The following salts are characteristic:

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[1] Curtius, *Journ. Prakt. Chem.* [2] xxvi. 145.

[2] Otto, *Ann. Chem. Pharm.* cxxxiv. 303.

[3] Jaffé, *Ber. Deutsch. Chem. Ges.* x. 1925; xi. 406.

Calcium ornithurate, $(C_{19}H_{19}N_2O_4)_2Ca$, is obtained by adding the ammonium salt to a solution of calcium chloride and heating the mixture; it is a crystalline precipitate, which is only very slightly soluble in water.

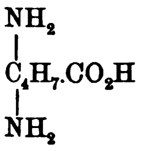
Barium ornithurate, $(C_{19}H_{19}N_2O_4)_2Ba$, is exceptionally soluble in water and alcohol, and is deposited from its alcoholic solution in opaque, crystalline flocks, which after drying form a snow-white powder.

On boiling the acid with hydrochloric acid, it decomposes almost immediately into benzoic acid and *benzoylornithine*, $C_{12}H_{16}N_2O_3$, which is almost insoluble in alcohol and crystallizes from water in very brittle needles, melting at 225° – 230°. It forms readily soluble salts with the mineral acids.

If the boiling with hydrochloric acid be continued for some time, the acid decomposes into benzoic acid and *ornithine*, $C_5H_{12}N_2O_2$, which is very deliquescent, has a strongly alkaline reaction and a somewhat caustic taste. It combines with acids to form salts which crystallize well.

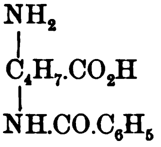
Ornithine has the composition of a diamidovalerianic acid, and the constitution of these compounds can therefore be expressed by the following formulæ:

Ornithine.



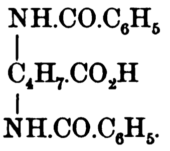
$$\begin{array}{l} NH_2 \\ | \\ C_4H_7.CO_2H \\ | \\ NH_2 \end{array}$$

Benzoylornithine.



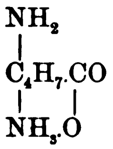
$$\begin{array}{l} NH_2 \\ | \\ C_4H_7.CO_2H \\ | \\ NH.CO.C_6H_5 \end{array}$$

Ornithuric acid.



$$\begin{array}{l} NH.CO.C_6H_5 \\ | \\ C_4H_7.CO_2H \\ | \\ NH.CO.C_6H_5. \end{array}$$

Free ornithine, which has an alkaline reaction, will, of course, have the following formula:



$$\begin{array}{l} NH_2 \\ | \\ C_4H_7.CO \\ |\qquad | \\ NH_3.O \end{array}$$

NITRIL AND ITS DERIVATIVES.

itril, $C_6H_5.CN$. This substance was prepared by
ller by heating benzamide with baryta,[1] but was
by them, and its identity with the benzonitril
ehling was established at a much later period.
st obtained it by the dry distillation of ammo-
from which it is formed by loss of water.
red by a similar reaction from benzamide,
y heating it with phosphorus pentoxide,[3] phos-
ride,[4] phosphorus pentasulphide,[5] benzoyl chlo-
benzoate,[7] or caustic lime.[8]
other methods of preparation, some of which
dy mentioned (Part III., p. 31), the following
ortant. It can readily be obtained by distilling
benzoic acid with one molecule of potassium

$$)_2H + HSCN = C_6H_5.CN + CO_2 + H_2S.$$

e benzoic acid is converted into the potassium
t can readily be recovered.[9]
te may be substituted for the potassium salt:[10]

$$Pb(SCN)_2 = 2C_6H_5.CN + PbS + H_2S + 2CO_2.$$

synthetically prepared by the distillation of
lphonate with potassium cyanide,[11] as well as
nzene to 350° with silver cyanide,[12] or by the
chloride on benzene in presence of aluminium
obtained from aniline by converting the latter
chloride and heating this with a solution of

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hem. *Pharm.* cxcii. 362.
[2] *Ibid.* xlix. 91.
uckton, *ibid.* c. 155.
Org. iv. 762; Henke, *Ann. Chem. Pharm.* cvi. 276.
utsch. *Chem. Ges.* ii. 307.
rdt's *Org. Chim.* i. 386.
utsch. *Chem. Ges.* vi. 113.
ulz, *Ann. Chem. Pharm.* cxcvi. 48.
ch. *Chem. Ges.* v. 673.
1766.
hem. 1868, 33; *Ber. Deutsch. Chem. Ges.* iii. 710.
ibid. x. 746.
s, *Bull. Soc. Chim.* xxix. 2.

BENZENYL COMPOUNDS.

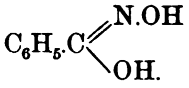
2113 These compounds are closely allied to the benzoyl derivatives. Phosphorus chloride converts benzoic acid, $C_6H_5.CO.OH$, first into benzoyl chloride, $C_6H_5.COCl$, and then by further action into benzenyl chloride, $C_6H_5.CCl_3$. The latter is also formed by the continued action of chlorine on boiling toluene; on heating with caustic potash it is reconverted into benzoic acid, which therefore bears the same relation to it as formic acid to chloroform. The action of the potash is probably to form *benzenyl alcohol* or *orthobenzoic acid* in the first instance:

$$C_6H_5.CCl_3 + 3KOH = C_6H_5.C(OH)_3 + 3KCl.$$

This is, however, as unstable as orthoformic acid and immediately decomposes into water and benzoic acid; ethers are, however, known, such as *ethyl orthobenzoate*, $C_6H_5.C(OC_2H_5)_3$, obtained by the action of sodium ethylate on benzenyl trichloride.

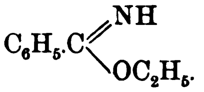
Benzoic acid itself may, therefore, be looked upon as a benzenyl compound, and this view was actually taken by Berzelius (Part I., p. 12).

A large number of compounds which are formed by the action of hydroxylamine on benzoyl chloride may also be included among the benzenyl derivatives. The simplest of these is benzyhydroxamic acid:



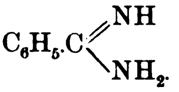
$$C_6H_5.C\begin{matrix}\diagup N.OH \\ \diagdown OH.\end{matrix}$$

Benzonitril, $C_6H_5.CN$, and its compounds with alcohols, such as benzimido-ethyl ether:



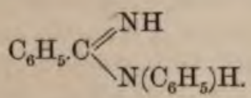
$$C_6H_5.C\begin{matrix}\diagup NH \\ \diagdown OC_2H_5.\end{matrix}$$

also belong to this class. The latter compound is converted by ammonia into benzenylamidine or benzimido-amide:



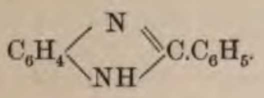
$$C_6H_5.C\begin{matrix}\diagup NH \\ \diagdown NH_2.\end{matrix}$$

Benzenyl amidines which contain the radical phenyl, &c., are obtained by heating benzonitril with the hydrochlorides of amido-bases; thus aniline yields phenylbenzenylamidine:



$$C_6H_5.C\begin{matrix}\diagup NH \\ \diagdown N(C_6H_5)H.\end{matrix}$$

Another series of amidines (Part III., p. 216) consists of the anhydro-bases, which are formed from the orthoamido-compounds by the elimination of water; benzoylorthodiamidobenzene in this way yields phenylenebenzenylamidine:



Benzenyl trichloride or *Benzo-trichloride*, $C_6H_5.CCl_3$. Liebig and Wöhler found during their researches on the radical of benzoic acid, that benzoyl chloride is converted by phosphorus pentachloride into a strongly-smelling, oily substance, which they did not investigate more closely.[1] It was made the subject of research by Schischkow and Rösing[2] and also by Limpricht,[3] who found that it is also formed when benzidene dichloride, $C_6H_5.CHCl_2$, is treated with chlorine, and named it benzoic trichloride. Benzenyl trichloride is most readily obtained by passing chlorine into boiling toluene until no further increase in weight takes place.[4] The product is then washed with caustic soda solution, dried over ignited potassium carbonate and rectified; it is employed in the colour industry and is manufactured on the large scale, being purified by distillation in a vacuum.

Benzenyl trichloride, which is also known as phenylchloroform, is a powerfully refractive liquid, which has a characteristic penetrating odour, boils at 213°—214°, and has a sp. gr. of 1·380 at 14°. On heating with water to 150°, it is converted into benzoic acid, while benzoic anhydride is formed when it is heated with sulphuric acid which contains 4·6 per cent. of water (p. 166). It is decomposed by fuming nitric acid with formation of metanitrobenzoic acid (Beilstein and Kuhlberg).

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[1] *Ann. Chem. Pharm.* iii. 265.
[2] *Jahresber. Chem.* 1858, 279.
[3] *Ann. Chem. Pharm.* cxxxiv. 55; cxxxv. 80; cxxxix. 323.
[4] Beilstein and Kuhlberg, *ibid.* cxlvi. 330.

Benzenyl tribromide, $C_6H_5.CBr_3$, is formed by the action of bromine on boiling toluene, and is a colourless liquid which has an exceedingly violent action on the eyes and mucous membrane. It cannot be distilled, since it decomposes at about 150°; on heating with water it is readily converted into benzoic acid, while it is only very slowly attacked by boiling alcohol.[1]

Benzenyl ethyl ether, $C_6H_5.C(OC_2H_5)_3$. This compound, which is also called ethyl orthobenzoate, was obtained by Limpricht, who heated the chloride to 100° with a solution of sodium in absolute alcohol. It is a transparent, colourless liquid, which smells like ethyl benzoate and boils at 220°–225°.

Benzenyl triacetate, $C_6H_5.C(OC_2H_3O)_3$, is formed by the action of silver acetate on the chloride, and is a liquid which decomposes on distillation into acetic anhydride and benzoic anhydride. If it be allowed to stand in the air or over sulphuric acid in a vacuum, white needles separate out, which melt at 70°, and have the composition of acetobenzoic anhydride (Limpricht).

Monochlorobenzenyl trichloride, $C_6H_4Cl.CCl_3$. The ortho-compound has been obtained by the action of phosphorus pentachloride on salicylic acid, $C_6H_4(OH)CO_2H$; it is crystalline, melts at 30° and boils at 260°.[2] The meta-compound has been prepared in a similar manner from metasulphobenzoic acid, $C_6H_4(SO_3H)CO_2H$, and boils at 235°;[3] the para-compound is formed by the chlorination of benzenyl trichloride in presence of iodine; it boils at 245° and yields parachlorobenzoic acid when heated with water to 200° (Beilstein and Kuhlberg).

Dichlorobenzenyl trichloride, $C_6H_3Cl_2.CCl_3$, has been prepared by the action of chlorine on a boiling mixture of the dichlorotoluenes obtained by chlorinating toluene. The product boils at 273°—280° and yields three dichlorobenzoic acids on heating with water.[4]

Trichlorobenzenyl trichloride, $C_6H_2Cl_3.CCl_3$, is formed by passing chlorine into boiling trichlorotoluene; it crystallizes from alcohol in very fine needles, melts at 82° and boils at 307°—308°.

Tetrachlorobenzenyl trichloride, $C_6HCl_4.CCl_3$, forms fine, short needles, melts at 104° and boils at 316°.[5]

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[1] Ince, *Abst. Proc. Chem. Soc.* 1885-6, 131.

[2] Kolbe and Lautemann, *Ann. Chem. Pharm.* cxv. 195.

[3] Carius and Kämmerer, *ibid.* cxxxviii. 58.

[4] Schulz, *ibid.* clxxxvii. 260; Aronheim and Dietrich, *Ber. Deutsch. Chem Ges.* viii. 1401.

[5] Beilstein and Kuhlberg, *Ann. Chem. Pharm.* cl. 286.

BENZONITRIL AND ITS DERIVATIVES.

2114 *Benzonitril*, $C_6H_5.CN$. This substance was prepared by Liebig and Wöhler by heating benzamide with baryta,[1] but was not investigated by them, and its identity with the benzonitril discovered by Fehling was established at a much later period. The latter chemist obtained it by the dry distillation of ammonium benzoate,[2] from which it is formed by loss of water. It can be prepared by a similar reaction from benzamide, $C_6H_5.CO.NH_2$, by heating it with phosphorus pentoxide,[3] phosphorus pentachloride,[4] phosphorus pentasulphide,[5] benzoyl chloride,[6] potassium benzoate,[7] or caustic lime.[8]

Among many other methods of preparation, some of which have been already mentioned (Part III., p. 31), the following are the most important. It can readily be obtained by distilling two molecules of benzoic acid with one molecule of potassium thiocyanate:

$$C_6H_5.CO_2H + HSCN = C_6H_5.CN + CO_2 + H_2S.$$

One half of the benzoic acid is converted into the potassium salt, from which it can readily be recovered.[9]

Lead thiocyanate may be substituted for the potassium salt:[10]

$$2C_6H_5.CO_2H + Pb(SCN)_2 = 2C_6H_5.CN + PbS + H_2S + 2CO_2.$$

Benzonitril is synthetically prepared by the distillation of sodium benzenesulphonate with potassium cyanide,[11] as well as by heating iodobenzene to 350° with silver cyanide,[12] or by the action of cyanogen chloride on benzene in presence of aluminium chloride.[13] It is obtained from aniline by converting the latter into diazobenzene chloride and heating this with a solution of the double cyanide of potassium and copper.[1] It can easily be prepared in the pure state by distilling benzamide with phosphorus pentoxide and rectifying the product over the latter. A good yield is obtained by Letts's process, according to which the mixture of benzoic acid and potassium thiocyanate is heated in an apparatus connected with an inverted condenser until a white, solid mass has been formed. The product is then distilled, the distillate freed from benzoic acid by means of ammonia, and the benzonitril finally distilled in steam; he thus obtains 80 per cent. of the theoretical yield. Merz, by the distillation of 500 grms. of sodium benzenesulphonate with 330 grms. of potassium cyanide, obtained in one case 130 and in another 140 grms. of the crude 80 per cent. nitril, while Henry, employing his own method, obtained half the theoretical yield.

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[1] Wöhler, *Ann. Chem. Pharm.* cxcii. 362.

[2] *Ibid.* xlix. 91.

[3] Hofmann and Buckton, *ibid.* c. 155.

[4] Gerhardt, *Chim Org.* iv. 762; Henke, *Ann. Chem. Pharm.* cvi. 276.

[5] Henry, *Ber. Deutsch. Chem. Ges.* ii. 307.

[6] Sokolow, *Gerhardt's Org. Chim.* i. 386.

[7] Kekulé, *Ber. Deutsch. Chem. Ges.* vi. 113.

[8] Anschütz and Schulz, *Ann. Chem. Pharm.* cxcvi. 48.

[9] Letts, *Ber. Deutsch. Chem. Ges.* v. 673.

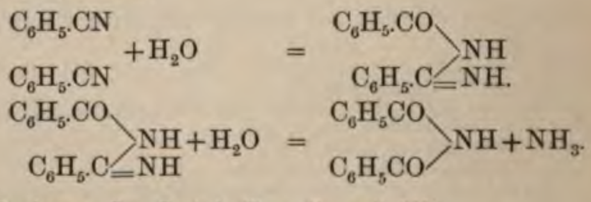
[10] Krüss, *ibid.* xvii. 1766.

[11] Merz, *Zeitschr. Chem.* 1868, 33; *Ber. Deutsch. Chem. Ges.* iii. 710.

[12] Merz and Weith, *ibid.* x. 746.

[13] Friedel and Crafts, *Bull. Soc. Chim.* xxix. 2.

Properties.—Benzonitril is a mobile liquid, which smells like oil of bitter almonds, has a sp. gr. of 1·023 at 0°, boils at 191° and solidifies in a mixture of ether and solid carbon dioxide to a crystalline mass, melting at −17°.[2] It is miscible with alcohol and ether, and dissolves in about 100 parts of water (Fehling). On boiling with caustic potash it is converted into benzoic acid, and it is reduced in alcoholic solution by zinc and hydrochloric acid to benzylamine (Mendius); fuming sulphuric acid in the cold polymerizes it to cyanphenin, but on heating, forms metasulphobenzoic and benzenedisulphonic acids (Hofmann and Buckton). When it is mixed with benzene and concentrated sulphuric acid, *dibenzimido-oxide*, $C_{14}H_{12}N_2O$, is obtained; it crystallizes in thick vitreous prisms and has basic properties.[3] On heating it with dilute hydrochloric acid, dibenzamide is formed.[4] Both substances are obtained when well-cooled, fuming sulphuric acid is allowed to drop into benzonitril, and the mixture treated with water after standing for some time.[5] Their formation is explained by the following equations:



$$\begin{array}{l}C_6H_5.CN\\ C_6H_5.CN\end{array} + H_2O = \left.\begin{array}{l}C_6H_5.CO\\ C_6H_5.C{=}NH.\end{array}\right> NH$$

$$\left.\begin{array}{l}C_6H_5.CO\\ C_6H_5.C{=}NH\end{array}\right> NH + H_2O = \left.\begin{array}{l}C_6H_5CO\\ C_6H_5CO\end{array}\right> NH + NH_3.$$

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[1] Sandmeyer, *Ber. Deutsch. Chem. Ges.* xvii. 2653.
[2] Hofmann, *Jahresber.* 1862, 335.
[3] Klein and Pinner, *Ber. Deutsch. Chem. Ges.* xi. 764.
[4] Pinner, *ibid.* xvii. 2006.
[5] Gumpert, *Journ. Prakt. Chem.* [2] xxx. 87; Pinner, *ibid.* xxx. 125.

When benzonitril is shaken up with a warm mixture of caustic potash solution and hydrogen peroxide, it is rapidly converted into benzamide, pure oxygen being evolved:[1]

$$C_6H_5.CN + 2H_2O_2 = C_6H_5.CO.NH_2 + H_2O + O_2.$$

If benzonitril be taken internally, it appears in the urine in the form of oxybenzonitrilsulphuric acid, $C_6H_4(O.SO_3H)CN$, which readily decomposes into sulphuric acid and the nitrils of salicylic acid and parahydroxybenzoic acid; the meta-compound, however, is not formed.[2]

Benzonitril combines with hydrobromic acid to form the crystalline compound, $C_6H_5.CN + 2HBr$, which is converted by water into benzamide:[3]

$$C_6H_5.CBr_2.NH_2 + H_2O = C_6H_5.CO.NH_2 + 2HBr.$$

According to Henry, a similar compound is formed with hydriodic,[4] but not with hydrochloric acid; when, however, a current of the latter gas is passed into an ethereal solution of platinum chloride and benzonitril, long needles separate out, which decompose in dry air into their three components.[5]

When benzonitril is heated with bromine, the monobromide, $(C_7H_5NBr)_2$, is formed; it crystallizes from ether in small needles, which partially sublime when heated and are partially decomposed into bromine, benzonitril and cyanphenin; while on heating with lime, some carbon dioxide and ammonia are evolved in addition to the compounds mentioned. A dibromide also appears to exist, but it is very unstable.[6]

It combines with some metallic chlorides to form the following solid compounds, $C_7H_5N,AuCl_3$, $(C_7H_5N)_2PtCl_4$, $(C_7H_5N)_2SnCl_4$ and $(C_7H_5N)_2TiCl_4$, the last of which forms bright crystals which may be sublimed.[7]

2115 *Cyanphenin*, $C_{21}H_{15}N_3$. This compound, which corresponds to cyanethin (Part I., p. 562), was obtained by Cloez by heating benzoyl chloride with potassium cyanate,[8] and Engler prepared it, as already mentioned, from benzonitril bromide. Hofmann found that it is formed when benzonitril is heated with sodium,[1] and Klein and Pinner when it is treated with fuming sulphuric acid.[2] It is also obtained in tolerable quantity, according to Henry, together with benzonitril, by the action of phosphorus pentasulphide on benzamide, and, together with an oily base, $C_{16}H_{18}N_2$, the hydrochloride of which, $C_{16}H_{19}N_2Cl$, crystallizes in six-sided tablets, when benzonitril is heated with zinc ethyl.[3]

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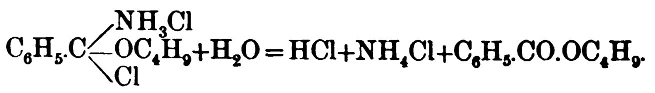
[1] Radziszewski, *Ber. Deutsch. Chem. Ges.* xviii. 355.
[2] Baumann, *ibid.* xvii. Ref. 256.
[3] Engler, *Ann. Chem. Pharm.* cxlix. 307.
[4] *Bull. Soc. Chim.* vii. 85.
[5] Klein and Pinner, *Ber. Deutsch. Chem. Ges.* x. 1891.
[6] Engler, *Ann. Chem. Pharm.* cxxxiii. 144.
[7] Henke, *ibid.* cvi. 284.
[8] *Ibid.* cxv. 27.

Cyanphenin is a hard, crystalline substance, which melts at 231°, sublimes in needles, and boils above 350°. It is insoluble in water, slightly soluble in alcohol and ether, more readily in carbon disulphide and ethyl iodide. It is not attacked when heated with aqueous or alcoholic potash, but is converted into benzoic acid by heating to 220°[4] with fuming hydriodic acid, or to 250° with concentrated hydrochloric acid (Frankland and Evans).

BENZIMIDO-ETHERS.

2116 *The Benzimido-ethers* include the compounds which are formed by the action of hydrochloric acid on a mixture of benzonitril with an alcohol. Of these compounds the isobutyl ether has been more fully described;[5] its formation is preceded by that of a compound which forms large, lustrous crystals, which fume in moist air and decompose into hydrochloric acid, ammonium chloride and isobutyl benzoate:



$$C_6H_5.C\begin{cases}NH_3Cl\\OC_4H_9\\Cl\end{cases}+H_2O=HCl+NH_4Cl+C_6H_5.CO.OC_4H_9.$$

If, however, the compound be freed from benzonitril and isobutyl alcohol by washing with ether and allowed to stand over caustic soda, a molecule of hydrochloric acid is given off and the hydrochloride of benzimido-isobutyl ether remains behind; it decomposes on heating into benzamide and isobutyl chloride:

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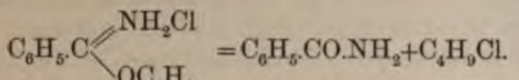
[1] *Ber. Deutsch. Chem. Ges.* i. 198.

[2] *Ibid.* xi. 764; Pinner, *Journ. Prakt. Chem.* [2] xxx. 125.

[3] Frankland and Evans, *Journ. Chem. Soc.* 1880, i. 563.

[4] Engler, *Ann. Chem. Pharm.* cxlix. 310.

[5] Pinner and Klein, *Ber. Deutsch. Chem. Ges.* x. 1889; xi. 4.



$$C_6H_5.C\left\langle\begin{matrix}NH_2Cl\\ OC_4H_9\end{matrix}\right. = C_6H_5.CO.NH_2 + C_4H_9Cl.$$

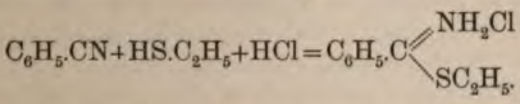
It is decomposed by a solution of ammonia in absolute alcohol, with formation of the free isobutyl ether, ammonium chloride and benzenylamidine hydrochloride.

Benzimido-isobutyl ether, $C_6H_5.C(NH)OC_4H_9$, is a thick, oily liquid, which partially decomposes on distillation; it readily recombines with hydrochloric acid; cold, concentrated sulphuric acid converts the hydrochloride into the acid sulphate, $C_6H_5C(OC_4H_9)NH_2.SO_4H$, which crystallizes in long, pliant needles.

Benzimido-acetic ether, $C_6H_5.C(NH)OC_2H_3O$, is formed by boiling the isobutyl ether with acetic anhydride; it is insoluble in water and acids, dissolves in alcohol and crystallizes in needles, melting at 116°.

Benzimido-ethyl ether, $C_6H_5.C(NH)OC_2H_5$. The hydrochloride of this compound forms large, lustrous, transparent prisms, which decompose at 118°—120° with formation of benzamide. In other respects the compound resembles its isobutyl analogue.[1]

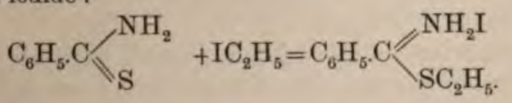
Benzimido-thio-ethyl ether, $C_6H_5.C(NH)SC_2H_5$. The hydrochloride of this compound is formed when hydrochloric acid is passed into a mixture of ethyl mercaptan and benzonitril:



$$C_6H_5.CN + HS.C_2H_5 + HCl = C_6H_5.C\left\langle\begin{matrix}NH_2Cl\\ SC_2H_5.\end{matrix}\right.$$

It crystallizes in thick prisms, which melt at 188° and are readily soluble in water and alcohol.

The hydriodide is obtained by heating thiobenzamide to 100° with ethyl iodide:



$$C_6H_5.C\left\langle\begin{matrix}NH_2\\ S\end{matrix}\right. + IC_2H_5 = C_6H_5.C\left\langle\begin{matrix}NH_2I\\ SC_2H_5.\end{matrix}\right.$$

It forms long, monosymmetric prisms, melting at 142.° Alkalis separate the ether from these salts as a strongly-smelling, oily liquid, which is soluble in water and readily decomposes into benzonitril and mercaptan.[2]

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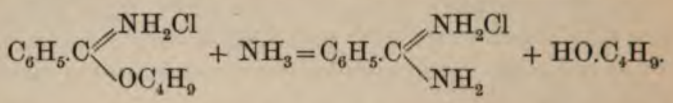
[1] Pinner, *Ber. Deutsch. Chem. Ges.* xvi. 1654.

[2] Bernthsen, *Ann. Chem. Pharm.* cxcvii 348.

Benzimido-thiobenzyl ether, $C_6H_5.C(NH)S.CH_2.C_6H_5$. The hydrochloride is obtained by the action of benzyl chloride on thiobenzamide, or of hydrochloric acid on a mixture of benzyl hydrosulphide and benzonitril. It is soluble in water and alcohol, and crystallizes in white tablets melting at 181°. The free base is very unstable (Bernthsen).

BENZENYLAMIDINES.

2117 *Benzenylamidine* or *Benzimido-amide*, $C_6H_5.C(NH)NH_2$, is formed, as already mentioned, by the action of alcoholic ammonia on the hydrochloride of benzimido-isobutyl ether:

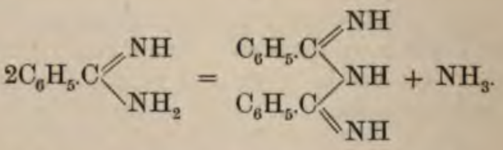


$$C_6H_5.C\begin{matrix} = NH_2Cl \\ - OC_4H_9 \end{matrix} + NH_3 = C_6H_5.C\begin{matrix} = NH_2Cl \\ - NH_2 \end{matrix} + HO.C_4H_9.$$

Free benzimido-isobutyl ether is simultaneously formed, but the quantity of this product diminishes when the temperature at which the reaction is carried out is raised.[1] The product is evaporated in a vacuum, the residue washed with ether and crystallized from alcohol, yielding benzenylamidine hydrochloride in flat needles, which are decomposed by caustic potash but not by ammonia; by shaking out with ether and evaporating, the free base is obtained as a crystalline mass, which is slightly soluble in water, readily in alcohol and has an alkaline taste and reaction. It decomposes spontaneously after some time with evolution of ammonia, which is also given off on heating, benzonitril and cyanphenin being formed.

If it be heated to 100° with ethyl iodide, the product decomposed with caustic soda and extracted with ether, *ethylbenzenylamidine*, $C_6H_5C(NC_2H_5)NH_2$, is obtained as a strongly alkaline, thick, oily liquid.

Dibenzenyltriamine, $C_{14}H_{13}N_3$, is formed, together with acetamide, when benzenylamidine is boiled with acetic anhydride:



$$2C_6H_5.C\begin{matrix} = NH \\ - NH_2 \end{matrix} = \begin{matrix} C_6H_5.C = NH \\ \quad > NH \\ C_6H_5.C = NH \end{matrix} + NH_3.$$

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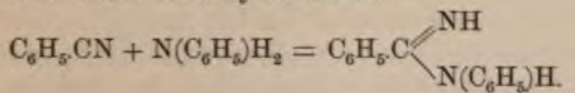
[1] Pinner and Klein, *Ber. Deutsch. Chem. Ges.* x. 1889.

It crystallizes in long, flat needles, which melt at 108°—109° and are not decomposed even at 240°.[1]

Phenylbenzenylamidine, $C_6H_5.C(NH)N(C_6H_5)H$, is obtained, together with diphenylbenzenylamidine, by heating benzonitril to 220°—240° with aniline hydrochloride:

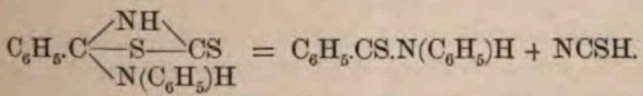


$$C_6H_5.CN + N(C_6H_5)H_2 = C_6H_5.C\left\langle\begin{array}{l}NH\\ N(C_6H_5)H.\end{array}\right.$$

The product is extracted with cold water and the solution precipitated with ammonia; the base thus obtained is very readily soluble in alcohol, and crystallizes badly in small crusts or warts composed of plates, which melt at 111°—112°, and, on further heating, partially sublime and are partially decomposed into aniline and benzonitril.

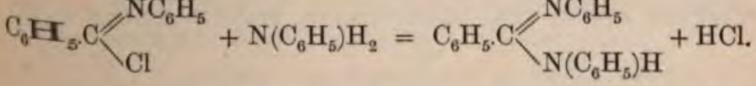
Phenylbenzenylamidine hydrochloride is a syrup, miscible with water and alcohol in all proportions.[2] It is converted by the action of sodium amalgam on its alcoholic solution into benzidenephenyldiamine, $C_6H_5.CH(NH_2)N(C_6H_5)H$.[3]

When phenylbenzenylamidine is heated with carbon disulphide, its thiocyanate is obtained together with thiobenzanilide; an intermediate product is probably first formed and then decomposed at the higher temperature:[4]



$$C_6H_5.C\left\langle\begin{array}{l}NH\diagdown\\ -S-CS\\ N(C_6H_5)H\end{array}\right. = C_6H_5.CS.N(C_6H_5)H + NCSH.$$

Symmetric diphenylbenzenylamidine, $C_6H_5.C(NC_6H_5)N(C_6H_5)H$. This compound was first prepared by Gerhardt, who obtained it by warming benzanilide with phosphorus pentachloride and then heating the product with aniline.[5] The compound $C_6H_5.CCl_2.N(C_6H_5)H$ is first formed, and is converted, with loss of hydrochloric acid, into *benzanilidimidochloride*, which acts upon the aniline in the following manner:



$$C_6H_5.C\left\langle\begin{array}{l}NC_6H_5\\ Cl\end{array}\right. + N(C_6H_5)H_2 = C_6H_5.C\left\langle\begin{array}{l}NC_6H_5\\ N(C_6H_5)H\end{array}\right. + HCl.$$

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[1] *Ber. Deutsch. Chem. Ges.* xi. 4.
[2] Bernthsen, *Ann. Chem. Pharm.* clxxxiv. 348.
[3] Bernthsen and Szymanski, *Ber. Deutsch. Chem. Ges.* xiii. 917.
[4] Bernthsen, *Ann. Chem. Pharm.* cxcii. 31.
[5] *Ann. Chem. Pharm.* cviii. 217.

Benzanilidimidochloride crystallizes from petroleum ether in large, transparent, lustrous plates, melts at 39°—40°, and boils without decomposition at about 310°: water decomposes it rapidly, benzanilide being reproduced.[1]

Diphenylbenzenylamidine is also formed by the action of aniline on benzenyl trichloride,[2] and by heating benzanilide with aniline hydrochloride and phosphorus trichloride.[3] It is slightly soluble in water, readily in alcohol, and crystallizes in needles, melting at 144° (Wallach and Hoffmann). On heating with hydrochloric acid to 150°, it decomposes into benzoic acid and aniline, while on heating with sulphuric acid, thiobenzanilide and phenyl mustard oil are formed (Bernthsen). Its hydrochloride, $C_{19}H_{16}N_2ClH$, is only very slightly soluble in cold water and crystallizes from alcohol in needles.

Asymmetric diphenylbenzenylamidine, $C_6H_5C(NH)N(C_6H_5)_2$, is prepared by heating benzonitril with diphenylamine hydrochloride to 180°—190°. It is exceptionally soluble in alcohol and tolerably in ether, from which it crystallizes in thin, yellowish, alkaline, rhombic tablets, melting at 112°. It decomposes on boiling into diphenylamine and benzonitril; when it is heated with carbon disulphide, its thiocyanate is formed together with diphenylthiobenzanilide, $C_6H_5CS.N(C_6H_5)_2$. Its hydrochloride crystallizes in needles or monoclinic prisms, which are readily soluble in water (Bernthsen).

Diphenylparamidobenzenylamidine or *Carbotriphenyltriamine*, $C_{19}H_{17}N_3$, was first prepared by Hofmann by heating aniline with tetrachloromethane;[4] it is more readily formed, however, from tetrabromomethane.[5] Weith obtained it by heating paranitrobenzoic acid with aniline and phosphorus trichloride, and reducing the diphenylparanitrobenzenylamidine thus formed with tin and hydrochloric acid,[6] while Michler and Walder prepared it by the action of aniline on trichloromethylsulphonyl chloride, CCl_3SO_2Cl.[7] It is insoluble in water, slightly soluble in ether, and crystallizes in long tablets, melting at 198°. On distillation it decomposes into hydrocyanic acid, benzonitril, ammonia, aniline, and diphenylamine, while on heating with hydrochloric acid to 160°, aniline and paramidobenzoic acid are formed:

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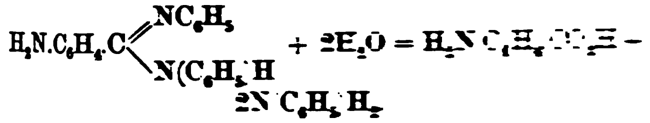
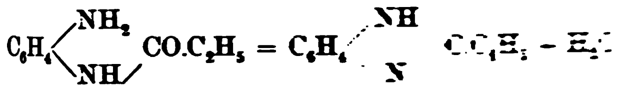
[1] Wallach and Hoffmann, *Ann. Chem. Pharm.* clxxxiv. 79.
[2] Limpricht, *ibid.* cxxxv. 82; Döbner, *Ber. Deutsch. Chem. Ges.* xv. 233.
[3] Hofmann, *Zeitschr. Chem.* 1866, 165.
[4] Hofmann, *Jahresber. Chem.* 1858, 351.
[5] Bolas and Groves, *Ann. Chem. Pharm.* clx. 178.
[6] *Ber. Deutsch. Chem. Ges.* xii. 101.
[7] *Ibid.* xiv. 2174.



$$H_2N.C_6H_4.C\begin{cases}NC_6H_5\\N(C_6H_5)H\end{cases} + 2H_2O = H_2N.C_6H_4.CO_2H + 2N(C_6H_5)H_2.$$

Phenylenebenzenylamidine, $C_{13}H_{10}N_2$, was termed anhydrobenzodiamidobenzene by Hübner, and is obtained by heating benzoylorthodiamidobenzene:

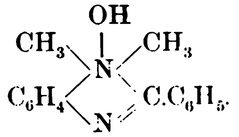


$$C_6H_4\begin{cases}NH_2\\NH\end{cases}CO.C_2H_5 = C_6H_4\begin{cases}NH\\N\end{cases}C.C_6H_5 + H_2O.$$

It may also be easily prepared by reducing benzoylorthonitroanilide with tin and hydrochloric acid, the rise of temperature caused by the reaction being sufficient to bring about the formation of the anhydro-base. It is slightly soluble in water, readily in alcohol, and crystallizes from glacial acetic acid in lustrous tablets, melting at about 280°; the hydrochloride, $C_{13}H_{10}N_2.ClH$ forms long needles, which are readily soluble in water.

The base is not attacked by benzoyl chloride even at 200°; on heating with iodine and alcohol, however, the periodide $C_{13}H_{10}N_2.IH.I_2$, is formed, and crystallizes in small plates which resemble iodine, but have a green surface lustre and are converted by boiling with water into the hydriodide, $C_{13}H_{10}N_2.IH + H_2O$, crystallizing in long, light yellow needles.

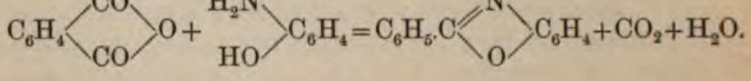
Dimethylphenylenebenzenylamide ammonium iodide, $C_{13}H_{10}N_2(CH_3)_2I$. When the anhydro-base is heated with methyl iodide to 180°, the periodide, $C_{13}H_{10}N_2(CH_3)_2I_3$, is formed: this substance crystallizes in long, brownish red needles, and is converted into the mono-iodide by boiling in alcoholic solution with freshly precipitated lead hydroxide. This compound crystallizes from hot water in long needles; caustic potash precipitates from its solution the hydroxide, $C_{13}H_{10}N_2(CH_3)_2OH$, in white flocks, which melt at 152° and are insoluble in water, but dissolve readily in hot alcohol. Its solution has a bitter taste, and its salts crystallize well; it has the following constitution:



Phenylenenitrobenzenylamidine, $C_{13}H_9(NO_2)N_2$, is obtained by dissolving the anhydro-base in fuming nitric acid; it crystallizes from alcohol in yellowish, microscopic needles, melting at 196°. It is reduced by tin and hydrochloric acid to *amidobenzenylphenylene-amidine*, $C_{13}H_9(NH_2)N_2$, which crystallizes from alcohol in small needles, melting at 240°. The hydrochloride, $C_{13}H_9(NH_2)N_2(ClH)_2$, forms small plates, which are very soluble in water; the sulphate, $C_{13}H_9(NH_2)N_2.SO_4H_2 + 2H_2O$, is only slightly soluble in hot water, and crystallizes in broad needles.

A large number of other similar anhydro-bases is also known.[1] The following compounds belong to the same class.

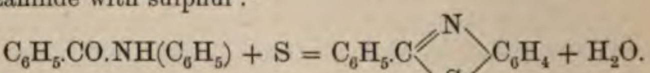
Benzenylamidophenate, $C_{13}H_9NO$. Ladenburg prepared this compound by heating ortho-amidophenol with benzoyl chloride, and by the distillation of the former with phthalic anhydride:



$$C_6H_4\left<\begin{matrix}CO\\CO\end{matrix}\right>O + \begin{matrix}H_2N\\HO\end{matrix}\!>C_6H_4 = C_6H_5.C\left<\begin{matrix}N\\O\end{matrix}\right>C_6H_4 + CO_2 + H_2O.$$

It crystallizes from dilute alcohol in lustrous plates, melts at 103°, and boils at 314°—317°; it combines with acids to form unstable salts; the platinichloride, $(C_{13}H_{10}NO)_2PtCl_6$, crystallizes from alcohol which contains hydrochloric acid in yellow prisms. On heating the base with concentrated hydrochloric acid to 150°, it decomposes into benzoic acid and orthamidophenol.[2]

Benzenylamidothiophenate, $C_{13}H_9NS$, is formed by boiling benzanilide with sulphur:[3]



$$C_6H_5.CO.NH(C_6H_5) + S = C_6H_5.C\left<\begin{matrix}N\\S\end{matrix}\right>C_6H_4 + H_2O.$$

It is also obtained by the action of benzoyl chloride on ortho-amidothiophenol, as well as by heating the latter with benzaldehyde, or benzonitril.[4] It is formed in smaller quantity, together with other products, when phenyl mustard oil is heated with benzoyl chloride.[5] It crystallizes from alcohol in needles, which, especially when heated, smell like tea-roses and geraniums, melt at 115°, and boil at about 360°. Like the preceding compound, it is a base and forms a platinichloride which crystallizes in long needles. It is not attacked when heated with concentrated hydrochloric acid to 200°; on fusion with caustic potash it is resolved into amidothiophenol and benzoic acid.

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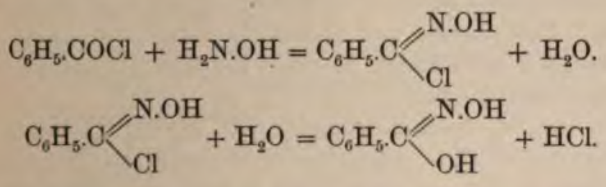
[1] Hübner, *Ann. Chem. Pharm.* ccviii. 278; ccix. 339; ccx. 328.
[2] *Ber. Deutsch. Chem. Ges.* ix. 1526.
[3] Hofmann, *ibid.* xii. 2359.
[4] *Ibid.* xiii. 1223.
[5] *Ibid.* xiii. 17.

BENZENYLOXIME COMPOUNDS.

2118 The three hydrogen atoms of hydroxylamine can, as was pointed out by Lossen, be successively replaced by benzoyl:

Benzhydroxylamine, $NOH_2(CO.C_6H_5)$,
Dibenzhydroxylamine, $NOH(CO.C_6H_5)_2$,
Tribenzhydroxylamine, $NO(CO.C_6H_5)_3$.

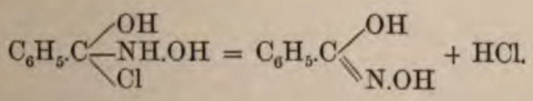
The last of these compounds is an indifferent substance; the two others are acids, and have therefore been called by Lossen benzhydroxamic acid and dibenzhydroxamic acid.[1] Certain cases of physical isomerism and of metamerism are characteristic of them and their derivatives. Lossen showed somewhat later that these peculiarities as well as numerous decompositions of the compounds in question can readily be explained if benzhydroxamic acid be looked upon as an oximido-compound of benzenyl;[2] its formation is then expressed by the following equations:



$$C_6H_5.COCl + H_2N.OH = C_6H_5.C\begin{matrix}N.OH\\Cl\end{matrix} + H_2O.$$

$$C_6H_5.C\begin{matrix}N.OH\\Cl\end{matrix} + H_2O = C_6H_5.C\begin{matrix}N.OH\\OH\end{matrix} + HCl.$$

It is, however, also possible that the hydroxylamine forms an additive compound with the benzoyl chloride, and that hydrochloric acid is then given off:[3]



$$C_6H_5.C\begin{matrix}OH\\NH.OH\\Cl\end{matrix} = C_6H_5.C\begin{matrix}OH\\N.OH\end{matrix} + HCl.$$

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[1] *Ann. Chem. Pharm.* clxi. 347.
[2] *Ber. Deutsch. Chem. Ges.* xvi. 873.
[3] *Ibid.* xviii. 1189.

The other compounds are then formed by the replacement of the hydrogen of the hydroxyls.

Hydroxylamine hydrochloride is dissolved in 8—10 parts of water, together with an equivalent amount of sodium carbonate, and 3 parts of benzoyl chloride gradually added, the whole being then well shaken up and cooled; the dibenzhydroxamic acid separates out together with a portion of the benzhydroxamic acid, which is removed by recrystallization from hot alcohol. The benzhydroxamic acid remaining in the solution is precipitated by barium chloride, and then liberated from the well-washed precipitate by dilute sulphuric acid. A further quantity of it can be obtained, since dibenzhydroxamic acid splits up into benzoic acid and benzhydroxamic acid when heated with baryta water.

Benzhydroxamic acid or *Benzenyloximic acid*, $C_6H_5.C(OH)NOH$, crystallizes in rhombic plates or tablets, and dissolves in 44·5 parts of water at 6°, much more readily in tolerably warm water, very readily in alcohol and slightly in ether. It has an acid reaction, melts at 124°—125°, and undergoes a sudden, violent decomposition at a higher temperature. When heated with dilute hydrochloric acid, it decomposes into hydroxylamine and benzoic acid. It is monobasic, but forms acid salts with the alkali metals.

Acid potassium benzhydroxamate, $C_6H_5.C(OH)NOK+C_6H_5.C(OH)NOH$, is tolerably soluble in cold water, scarcely in alcohol, and crystallizes in small rhombic plates or flat, pointed prisms, which deflagrate sometimes with the production of flame, when heated. The normal salt is readily soluble in alcohol; on evaporation of the solution, however, the acid salt and potassium carbonate separate out.

Acid sodium benzhydroxamate, $C_6H_5.C(OH)NONa+C_6H_5.C(OH)NOH+3H_2O$, is somewhat more readily soluble in water, slightly in alcohol, and crystallizes in long, thin plates, or large elongated tablets, which rapidly deliquesce in the air.

Acid barium hydroxamate, $(C_7H_6NO_2)_2Ba+C_7H_7NO_2$, forms small prisms scarcely soluble in water and alcohol.

Normal barium hydroxamate, $(C_7H_6NO_2)_2Ba$, is ootained by the addition of barium chloride to a solution of the acid potassium salt which has been treated with ammonia; it forms microscopic needles. The calcium salt is a precipitate resembling alumina; the benzhydroxamates of most of the other metals are also insoluble.

The behaviour of the acid and its acid salts towards ferric chloride is very characteristic; a dark red precipitate is formed which dissolves in an excess of the precipitant with a deep cherry-red colour, which is not altered by the addition of dilute hydrochloric or sulphuric acid, but is destroyed by concentrated hydrochloric acid; the addition of water causes the reappearance of the colour. If the original solution contains hydrochloric acid, ferric chloride only produces a colouration.

When the barium salt is distilled with a little water aniline is formed:[1]

$$2(C_6H_5C(OH)NO)_2Ba + H_2O = 2C_6H_5.NH_2 + CO_2 + BaCO_3.$$

Ethyl benzhydroxamate, $C_6H_5.C(OH)OC_2H_5$, is obtained by the action of ethyl iodide and caustic potash on a solution of the acid in alcohol,[2] as well as by that of benzoyl chloride on ethyl hydroxylamine, $H_2N(OC_2H_5)$.[3] It is very slightly soluble in water, readily in alcohol, and crystallizes in thick tablets, which melt at 64°—65° and are resolved at 190° into alcohol, aldehyde, benzamide and phenyl isocyanate. It is readily soluble in alkalis, being re-precipitated from solution by acids and even by carbon dioxide; on heating with concentrated hydrochloric acid, it decomposes into benzoic acid and ethyl hydroxylamine. If equal molecules of the ether and caustic potash be dissolved in alcohol and treated with silver nitrate, a white precipitate of $C_6H_5.C(OAg)NOC_2H_5$, is obtained, which blackens only on heating, while silver benzhydroxamate blackens and decomposes immediately on precipitation.

Benzoyl ethylbenzhydroxamate, or *Benzethylbenzhydroxylamine*, $C_6H_5.C(O.CO.C_6H_5)NOC_2H_5$, is obtained by the action of benzoyl chloride on an alkaline solution of the ether; it is readily soluble in alcohol and ether and forms transparent rhombic crystals, melting at 48°—49°.[4]

2119 *Dibenzhydroxamic acid*, or *Benzoylbenzoximic acid*, $C_6H_5.C(OH)NO.CO.C_6H_5$, which is produced by the action of benzoyl chloride on benzhydroxamic acid, crystallizes from hot alcohol in needles, and on the spontaneous evaporation of the solution in large, lustrous, rhombic prisms; it has an acid reaction, melts at 153°,[5] and decomposes violently at a higher temperature with formation of carbon dioxide, benzoic acid, benzanilide and phenyl isocyanate.[6] On heating with hydrochloric acid it splits up into benzoic acid and hydroxylamine, while alkalis decompose it into benzhydroxamic acid and benzoic acid, so that the former acid can be prepared from it by means of baryta water. Its alkali salts on the other hand are decomposed by water even in the cold, more rapidly on heating, with formation of benzoic acid, carbon dioxide and diphenyl urea:

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[1] Ann. Chem. Pharm. clxxv. 323.

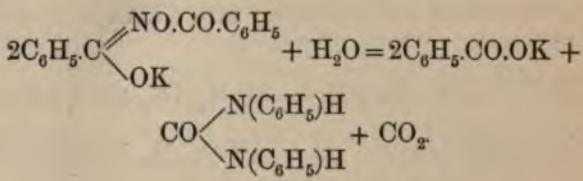
[2] Waldstein, *ibid.* clxxxi. 384.

[3] Gürke, *ibid.* ccv. 278.

[4] Pieper, *ibid.* ccxvii. 8.

[5] Steiner, *ibid.* clxxviii. 226.

[6] Pieschel, *ibid.* clxxv. 305.



$$2C_6H_5.C\left\langle\begin{matrix}NO.CO.C_6H_5\\OK\end{matrix}\right. + H_2O = 2C_6H_5.CO.OK + CO\left\langle\begin{matrix}N(C_6H_5)H\\N(C_6H_5)H\end{matrix}\right. + CO_2.$$

As already mentioned, benzhydroxamic acid can be directly converted into aniline, while dibenzhydroxamic acid yields derivatives of this—phenyl isocyanate, benzanilide and diphenyl urea—from which aniline can easily be obtained. Since the homologues of benzoic acid also yield oximes, a general method is established by which the carboxyl of a monobasic aromatic acid can be replaced by an amido-group (Lossen).

Inversely, the amido-group of amido-compounds can be replaced by carboxyl, and aniline thus converted into benzoic acid (Part III. p. 31).

Potassium dibenzhydroxamate, $C_6H_5.C(OK)NO.CO.C_6H_5$, is precipitated in thin plates when alcoholic solutions of the acid and caustic potash are mixed. If silver nitrate be added to its freshly prepared aqueous solution, a white precipitate of the silver salt is obtained; if this be dried, covered with ether and treated with ethyl iodide, the ethyl ether is obtained in two isomeric forms, one of which is an oily substance,[1] while the other is dimorphous.

a-Ethyl dibenzhydroxamate, $C_6H_5.C(OC_2H_5)NO.CO.C_6H_5$, is the chief product of the reaction; it is readily soluble in ether and alcohol, and crystallizes in four- or eight-sided rhombic prisms, melting at 58.°

β-Ethyl dibenzhydroxamate, which is only formed in very small quantity, is more readily soluble than the *a*-compound and forms triclinic crystals, melting at 63°.

These modifications cannot be directly converted into each ether; on heating they decompose into benzonitril, aldehyde and benzoic acid:

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[1] Eiseler, *Ann. Chem. Pharm.* clxxv. 326; Gürke, *ibid.* ccv. 279.

$$C_6H_5.C(OC_2H_5)NO.CO.C_6H_5 = C_6H_5.CN + C_2H_4O + C_6H_5CO.OH.$$

Concentrated hydrochloric acid decomposes them into benzoic acid, ethyl benzoate and hydroxylamine, while on heating with caustic potash, benzoic acid and two isomeric ethylhydroxamic acids are formed.

The oily ether is also readily soluble in alcohol and ether, and behaves chemically like the two others; it is only formed in small quantity and has not been closely investigated.

α-Ethylbenzhydroxamic acid, $C_6H_5.C(OC_2H_5)NOH$, is readily soluble in alcohol and ether; it crystallizes from a mixture of ether and benzene in monoclinic tablets or prisms, melting at 53·5°.

The ethyl ether, $C_6H_5.C(OC_2H_5)NOC_2H_5$, is formed by the action of ethyl iodide on a solution of the acid in alcoholic potash.[1] It is a powerfully refractive liquid which has a pleasant aromatic odour, and boils at 244° with slight decomposition; its vapour has a sp. gr. of 6·56 (Gürke). On heating with alcohol and hydrochloric acid, it forms ethyl benzoate and ethyl hydroxylamine.

β-Ethylhydroxamic acid is isomorphous with the α-compound, but it melts at 67·5°—68°, is more soluble in petroleum spirit, less so in caustic potash, and is more readily extracted from this by ether. Its ethyl ether is so similar to that of the α-compound that it is doubtful whether they are distinct substances.

Both acids are formed simultaneously by the action of hydroxylamine on benzimido-ethyl ether.[2]

It is almost completely converted into ethyl β-dibenzhydroxamate by the action of benzoyl chloride.[3]

2120 *Tribenzhydroxylamine*, or *Dibenzobenzoximate*, $C_6H_5.C(O.CO.C_6H_5)NO.CO.C_6H_5$, is obtained in three modifications by treating dry hydroxylamine hydrochloride with a solution of benzoyl chloride in toluene, or by heating potassium dibenzhydroxamate with benzoyl chloride.[4] It is, however, best prepared by acting upon silver dibenzhydroxamate with a solution of benzoyl chloride in petroleum ether, and allowing the whole to stand until the silver chloride has separated as a dense precipitate (Lossen).

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[1] Lossen and Zanni, *Ann. Chem. Pharm.* clxxxii. 220.

[2] Lossen, *Ber. Deutsch. Chem. Ges.* xvii. 1587.

[3] Gürke, *Ann. Chem. Pharm.* ccv. 281.

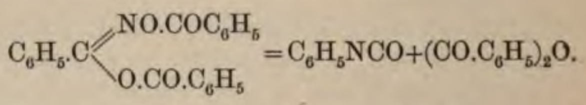
[4] Lossen, *Ann. Chem. Pharm.* clxi. 360; clxxv. 282; clxxxvi. 34; Steiner, *ibid.* clxxviii. 225.

α-Tribenzhydroxylamine is slightly soluble in cold, more readily in hot alcohol and ether, and forms monoclinic crystals, elongated in the direction of the ortho-diagonal,[1] which melt at 100°. It is completely split up into benzoic acid and dibenzhydroxamic acid by heating for an hour with hydrochloric acid of sp. gr. 1·05.

β-Tribenzhydroxylamine is insoluble in ether, slightly soluble in cold, more readily in hot alcohol, and forms small, lustrous, monoclinic crystals, melting at 141°—142° (Klein and Trechmann). It is decomposed by concentrated hydrochloric acid at 150° into benzoic acid, dibenzhydroxamic acid and hydroxylamine.

γ-Tribenzhydroxylamine is only formed in small quantity; it crystallizes in short, monoclinic prisms, melting at 112°, and is to a large extent converted into the β-compound by dilute hydrochloric acid.

All the three modifications are resolved on dry distillation into benzoic anhydride and phenyl isocyanate:

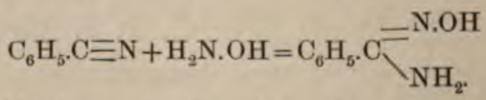


$$C_6H_5.C\begin{cases}NO.COC_6H_5\\O.CO.C_6H_5\end{cases} = C_6H_5NCO + (CO.C_6H_5)_2O.$$

They are decomposed by alcoholic potash into dibenzhydroxamic acid and benzoic acid.

The chemical behaviour of these substances is therefore identical, and they present an instance of trimorphism, for although they all crystallize in forms belonging to the monoclinic system, these forms are distinct ones and cannot be derived from one another.

Benzenylamidoxime, or *Benzhydroxamide*, $C_6H_5.C(NOH)NH_2$ is formed when a solution of hydroxylamine and benzonitril in dilute alcohol is heated to 80° for about eighteen hours:[2]



$$C_6H_5.C{\equiv}N + H_2N.OH = C_6H_5.C\begin{cases}N.OH\\NH_2.\end{cases}$$

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[1] Klein and Trechmann, *Ann. Chem. Pharm.* clxxxvi. 104.

[2] Krüger and Tiemann, *Ber. Deutsch. Chem. Ges.* xvii. 126, 1687; xviii. 727, 1053.

It is also formed by the action of hydroxylamine on benzamidine, $C_6H_5.C(NH)NH_2$, and was described by Pinner as *benzoxamidine.*[1]

It is readily soluble in alcohol and ether, and crystallizes from hot water in long, flat, acute prisms, melting at 79°—80°. It is precipitated by petroleum spirit from its solution in benzene in needles. Its solution is coloured deep red by ferric chloride; it forms salts both with acids and bases. Benzamide and nitrous oxide are formed by the action of sodium nitrite on its hydrochloride, while when heated to 200° with hydrochloric acid, it decomposes into ammonium chloride and benzoic acid.

Benzenylamidoxime is poisonous; thus, 0·5 grm. proved fatal to a dog, 0·1 grm. to a rabbit, and 0·03 grm. to a frog.

Its alkyl ethers are formed by heating the sodium salt with the corresponding iodide.

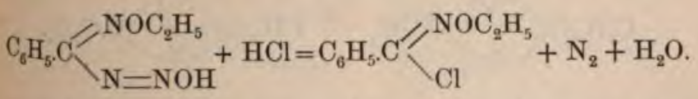
Ethyl ether of benzenylamidoxime, $C_6H_5.C(NOC_2H_5)NH_2$, is almost insoluble in water, but readily soluble in alcohol and ether, and crystallizes in rhombic plates, which melt at 67°, and dissolve in acids but not in alkalis. Its hydrochloride crystallizes well.

Benzenylethoxime chloride, $C_6H_5.C(NOC_2H_5)Cl$, is formed when sodium nitrite is added to a well-cooled solution of the ether:

$$C_6H_5.C(NOC_2H_5)NH_2 + HCl + NaNO_2 = C_6H_5.C(NOC_2H_5)OH \\ + NaCl + H_2O + N_2.$$

$$C_6H_5.C(NOC_2H_5)OH + HCl = C_6H_5(NOC_2H_5)Cl + H_2O.$$

According to Lossen, a diazo-compound is probably formed at first, and then decomposes in the following manner:[2]



$$C_6H_5.C\begin{cases}NOC_2H_5\\N{=}NOH\end{cases} + HCl = C_6H_5.C\begin{cases}NOC_2H_5\\Cl\end{cases} + N_2 + H_2O.$$

The chloride is also readily produced by the action of phosphorus pentachloride on ethyl benzhydroxamate, $C_6H_5.C(NOC_2H_5)OH$.[3] It is an oily, aromatic liquid, which boils at 239°, is not decomposed by water or alcohol, and is not even attacked when heated for a short time with acids and alkalis. When heated with alcoholic ammonia to 160°—180°, however, the amidoxime ethyl ether is re-formed, and it is converted by the action of a solution of sodium in absolute alcohol into ethyl ethylbenzhydroxamate.

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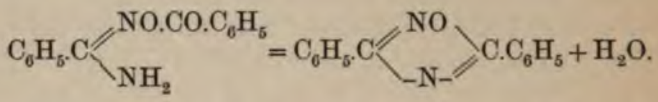
[1] Krüger and Tiemann, *Ber Deutsch. Chem. Ges.* xviii. 184.

[2] *Ber. Deutsch. Chem. Ges.* xviii. 1193.

[3] *Ibid.*

Benzoylbenzenylamidoxime, $C_6H_5.C(NO.CO.C_6H_5)NH_2$, is formed by the action of benzoyl chloride on benzenylamidoxime. It crystallizes in fine, white needles, which melt at 140°, and are soluble in alcohol, ether, and acids, but not in alkalis.

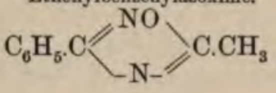
2121 *Dibenzenylazoxime*, $(C_7H_5)_2N_2O$, is obtained by heating the compound just described beyond its melting-point, or by treating it with dehydrating agents, such as benzoic anhydride or benzoyl chloride:



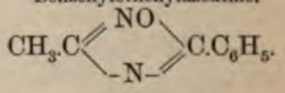
It is scarcely soluble in water, but readily in alcohol, and crystallizes in long, fine needles, which, after drying, resemble asbestos and melt at 108°, but sublime at a much lower temperature.

Ethenylbenzenylazoxime is formed by the action of acetic anhydride on benzenylamidoxime, and is very similar to the preceding compound, crystallizing in needles which readily sublime, have a characteristic odour and melt at 41°. It is isomeric with *benzenylethenylazoxime*, which is obtained by the action of benzoyl chloride on ethenylamidoxime, $CH_3.C(NOH)NH_2$, and forms aromatic needles, which melt at 57° and sublime very easily.[1] The isomerism of these two compounds is shown by the following formulæ:

Ethenylbenzenylazoxime.



Benzenylethenylazoxime.



Acetylbenzenylamidoxime, $C_6H_5.C(NO.CO.CH_3)NH_2$, is formed by the action of acetyl chloride on an ethereal solution of benzenylamidoxime. It crystallizes from alcohol in small plates or flat prisms, which melt at 96°, and are easily converted into ethenylbenzenylazoxime, the change being brought about even by boiling with water.[2]

Ethyl benzenylamidoximecarboxylate, $C_6H_5.C(NH_2)NO.CO.OC_2H_5$

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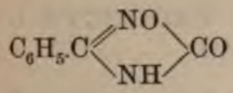
[1] Nordmann, *Ber. Deutsch. Chem. Ges.* xv. 2754.
[2] Schultz, *ibid.* xviii. 1080.

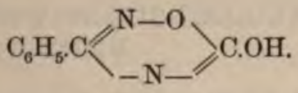
is obtained by adding ethyl chlorocarbonate to a solution of benzenylamidoxime in chloroform. It crystallizes in long, lustrous needles, which melt at 127° and are decomposed at a higher temperature, or on heating with water, into the following compound, alcohol being removed:

Benzenylazoxime carbinol, $C_8H_6N_2O_2$, is most simply prepared by heating benzenylamidoxime with ethyl chlorocarbonate. It crystallizes from hot water in long needles, melting at 197°. It readily dissolves in alkalis; its aqueous solution has an acid reaction and decomposes the carbonates of the alkaline earth metals. Silver nitrate precipitates the white crystalline silver salt from a solution neutralized with ammonia, and copper sulphate, the green copper salt, $(C_8H_5N_2O_2)_2Cu$.

According to the method by which it is prepared, benzenylazoxime carbinol should have the first of the following formulæ; its whole behaviour, however, corresponds with the second, and an intramolecular change must therefore be assumed:



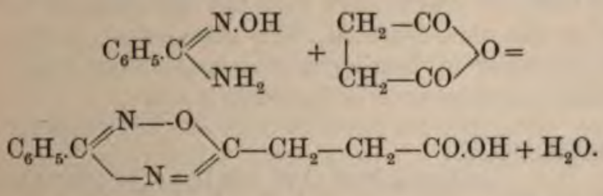
$$C_6H_5.C\left\langle\begin{matrix}NO\\NH\end{matrix}\right\rangle CO$$



$$C_6H_5.C\left\langle\begin{matrix}N-O\\-N-\end{matrix}\right\rangle C.OH.$$

Carbonyldibenzenylamidoxime, $(C_6H_5.C(NH_2)NO)_2CO$, is formed when benzenylamidoxime is brought into contact with carbonyl chloride dissolved in benzene. It is almost insoluble in the latter and is precipitated by water from its alcoholic solution in small plates, melting at 128°—129°. On heating with caustic soda solution, the preceding compound is formed.[1]

Benzenylazoxime propenylcarboxylic acid, $C_{11}H_{10}N_2O_3$, is obtained by heating benzenylamidoxime with succinic andydride:



$$C_6H_5.C\left\langle\begin{matrix}N.OH\\NH_2\end{matrix}\right. + \left.\begin{matrix}CH_2-CO\\|\\CH_2-CO\end{matrix}\right\rangle O =$$

$$C_6H_5.C\left\langle\begin{matrix}N-O\\-N=\end{matrix}\right\rangle C-CH_2-CH_2-CO.OH + H_2O.$$

It crystallizes from hot water in small, lustrous, white, rhombic plates or prisms, melting at 120°.

The anhydrides of other dibasic acids give similar compounds.[2]

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[1] Falck, *Ber. Deutsch. Chem. Ges.* xviii. 2467.

[2] Schultz, *ibid.* xviii. 2458.

Metanitrobenzenylamidoxime, $C_6H_4(NO_2)C(NH_2)NOH$. Metanitrobenzonitril readily combines with hydroxylamine to form this compound. It crystallizes in orange-coloured prisms, melting at 174°. A series of compounds has been prepared from it, corresponding to those described above.[1]

Metamidobenzenylamidoxime, $C_6H_4(NH_2)C(NH_2)NOH$, is formed by the reduction of the preceding compound, and separates from ether as a yellow oil which gradually solidifies. Its hydrochloride, $C_6H_4(NH_3Cl)C(NH_3Cl)NOH$, crystallizes from hot water in prisms.

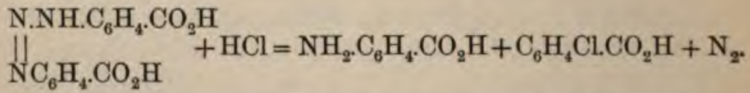
Metahydroxybenzenylamidoxime, $C_6H_4(OH)C(NH_2)NOH$, has been prepared from the amido-compound by the diazo-reaction, and crystallizes from dilute alcohol in light yellow needles, melting at 163°.[2]

HALOGEN-SUBSTITUTION PRODUCTS OF BENZOIC ACID.

2122 When an atom of hydrogen in benzoic acid is replaced by an element of the chlorine group, a meta-compound is formed, and not, as in the case of toluene and the benzyl compounds, a para-compound, accompanied by a small amount of an ortho-compound.

Substituted benzoic acids are obtained by the oxidation of the corresponding alcohols and aldehydes, as well as of the substitution products of toluene and such other compounds as are themselves readily oxidized to benzoic acid.

They may also be obtained from the amidobenzoic acids by means of the diazo-reaction. The old method, proposed by Griess, consisted in heating a diazo-amidobenzoic acid with hydrochloric, hydrobromic, or hydrofluoric acid:



$$\begin{array}{l}\mathrm{N.NH.C_6H_4.CO_2H}\\ \|\\ \mathrm{NC_6H_4.CO_2H}\end{array} + \mathrm{HCl} = \mathrm{NH_2.C_6H_4.CO_2H} + \mathrm{C_6H_4Cl.CO_2H} + \mathrm{N_2}.$$

He subsequently found that the sulphates of the diazobenzoic acids are more suitable for the purpose; one part is boiled with 3 to 5 parts of the hydracid, the substituted benzoic acid separating out on cooling as a mass of crystals. Hydriodic acid acts in this way even in the cold:[1]

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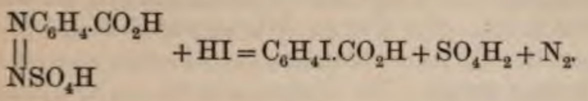
[1] Schöpff, *Ber. Deutsch. Chem. Ges.* xviii. 1063.

[2] *Ibid.* xviii. 2472.



$$\begin{matrix} NC_6H_4.CO_2H \\ \| \\ NSO_4H \end{matrix} + HI = C_6H_4I.CO_2H + SO_4H_2 + N_2.$$

A reaction which possesses considerable theoretical interest has been employed for the preparation of these compounds by v. Richter. When paranitrochlorobenzene or paranitrobromobenzene is heated with alcohol and potassium cyanide, the nitroxyl group is replaced by hydrogen, and the cyanogen group takes the meta-position, the nitril of metachloro- or metabromobenzoic acid being formed, while metanitrochlorobenzene is converted into orthochlorobenzoyl chloride. Orthonitrochlorobenzene and orthonitrobromobenzene, on the other hand, are not attacked by potassium cyanide.[2]

The halogen-substitution products are readily converted into benzoic acid by the action of sodium amalgam and water.

MONOCHLOROBENZOIC ACIDS, $C_6H_4Cl.CO_2H$.

2122 *Orthochlorobenzoic acid* was obtained by Chiozza in 1852, by heating salicylic acid (orthohydroxybenzoic acid) with phosphorus pentachloride, and decomposing the fraction of the distillate boiling between 200°—250° with water.[3] It was believed to be identical with the chlorobenzoic acid which is formed by the direct chlorination of benzoic acid, until Limpricht and Uslar, as well as Kolbe and Lautemann, showed that the latter compound is a distinct substance, and gave it a distinctive name, chlorosalylic acid.[4] Kekulé obtained the same acid in a similar manner from wintergreen oil, which consists chiefly of methyl salicylate.[5]

Its formation will be discussed under salicylic acid. In order to prepare it, an intimate mixture of one molecule of sodium salicylate with two molecules of phosphorus pentachloride is distilled, the portion boiling above 240° separated, and decomposed by boiling caustic soda solution, the acid being then precipitated by hydrochloric acid (Kolbe and Lautemann). The precipitate is dissolved in the smallest possible quantity of boiling water and treated with a slight excess of weak milk of lime; calcium salicylate is thus formed and separates completely when the solution is well stirred and heated on the water-bath for some hours. The filtrate is precipitated with hydrochloric acid and the orthochlorobenzoic acid purified by re-crystallization from boiling water.[1] The mixture of acids can also be separated by distillation with steam, with which salicylic acid alone volatilizes.[2]

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[1] *Ber. Deutsch. Chem. Ges.* xviii. 960.

[2] *Ibid.* iv. 459.

[3] *Ann. Chem. Pharm.* lxxxiii. 317.

[4] *Ibid.* cxv. 183.

[5] *Ibid.* cxvii. 145.

Pure salicylic acid may be substituted for the sodium salicylate.[3] According to Glutz it is better to employ wintergreen oil, to which the phosphorus pentachloride must be gradually added, the mixture heated for a considerable time until hydrochloric acid ceases to be evolved, and then distilled and treated as above.[4]

Orthochlorobenzoic acid is also formed when orthochlorotoluene is boiled with a dilute solution of potassium permanganate.[5] It dissolves in 881 parts of water at 0°, is readily soluble in hot water and alcohol, and crystallizes in long, silky needles, which melt at 137°, and sublime in lustrous crystals. It melts when heated with a little water, in the same manner as benzoic acid. When heated to 200° with caustic potash, it yields 10 per cent. of salicylic acid and 20 per cent. of metahydroxybenzoic acid, equal quantities being formed when caustic soda is employed (Ost).

Calcium orthochlorobenzoate, $(C_7H_4ClO_2)_2Ca + 2H_2O$, crystallizes in prisms, which are very slightly soluble in alcohol, but very readily in water. The solution of the acid in ammonia is therefore not precipitated by calcium chloride, and it may thus be distinguished from its isomerides.

Orthochlorobenzoyl chloride, $C_6H_4ClCOCl$, is obtained in the pure state by the action of phosphorus chloride on the acid. It is a heavy, powerfully refractive liquid which fumes in the air and boils at 235°—238° (Emmerling).

Orthochlorobenzonitril, C_6H_4ClCN, is formed by the action of phosphorus pentachloride on salicylamide, $C_6H_4(OH)CO.NH_2$. It crystallizes from hot water or ether in white needles, which smell like benzonitril and melt at 42°—43°. It sublimes readily, boils at 232°, and is converted into orthochlorobenzoic acid when heated to 150° with dilute hydrochloric acid.[1]

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[1] Beilstein and Reichenbach, *Ann. Chem. Pharm.* cxxxii. 311.

[2] Hübner and Upmann, *Zeitschr. Chem.* 1870, 293.

[3] Hübner and Biedermann, *Ann. Chem. Pharm.* cxlii. 263; Wilkens and Rack, *ibid.* ccxxii. 192.

[4] Glutz, *ibid.* cxliii. 194; Ost, *Journ. Prakt. Chem.* [2] xi. 386.

[5] Emmerling, *Ber. Deutsch. Chem. Ges.* viii. 880.

2124 *Metachlorobenzoic acid.* Herzog, in 1840, found that the action of chlorine upon benzoic acid produces, among other products, a chlorinated acid resembling benzoic acid, but he did not analyze the substance.[2] Scharling subsequently obtained an acid by the distillation of urine with hydrochloric acid, which had the composition of chlorobenzoic acid, and which he named *chloromichmic acid* (ὄμιχμα, urine),[3] but, as Gmelin pointed out, it was not to be distinguished from chlorobenzoic acid.[4] Stenhouse prepared the latter by treating benzoic or cinnamic acid with chlorine, bleaching powder or potassium chlorate and hydrochloric acid, but was unable to free it from higher chlorine substitution products.[5] Field, however, found that it can be obtained pure by boiling benzoic acid with potassium chlorate and hydrochloric acid, and this was confirmed by Otto.[6] As already mentioned, this acid was believed to be identical with the chlorobenzoic acid prepared from salicylic acid, until Limpricht and Uslar showed that the acid obtained in this way is different from that obtained by treating sulphobenzoic acid with phosphorus pentachloride, and decomposing the resulting chlorobenzoyl chloride with water.[7] The chlorobenzoic acids formed by these different reactions were made the subject of a close investigation by Beilstein and Schlun, which resulted in their proving the existence of three isomerides, the third of which had been obtained by Beilstein and Wilbrand from nitrodracylic acid (Part III. p. 34).[8]

Metachlorobenzoic acid was also obtained by Saint-Evre[9] by the action of chlorine on a solution of benzoic acid in caustic potash, and was named *chloroniceïnic acid*, $C_6H_5ClO_2$. It is also formed when benzoic acid is heated with antimony chloride and the product treated with water,[10] as well as by the oxidation of metachlorotoluene with chromic acid.[11]

In order to prepare it, potassium chlorate is gradually added to benzoic acid suspended in hydrochloric acid; the reaction, which proceeds quietly, must be occasionally aided by gentle warming. When 26 parts of chlorate have been added to 10 parts of the acid and about 90 parts of hydrochloric acid, the mixture is heated to boiling, and the acid which separates on cooling converted into the barium salt, which is then purified by re-crystallization.

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[1] Henry, *Ber. Deutsch. Chem. Ges.* vi. 492.
[2] Brandes, *Arch. Pharm.* xxiii. 15.
[3] *Ann. Chem. Pharm.* xli. 48; xlii. 265.
[4] *Handb. Org. Chem.* iii. 92.
[5] *Phil. Mag.* xxvii. 129; *Ann. Chem. Pharm.* lxv. 55.
[6] *Ibid.* cxxii. 142.
[7] *Ibid.* cii. 259.
[8] *Ibid.* cxxxiii. 293.
[9] *Ibid.* lxx. 257.
[10] Gerhardt, *Traité Chim. Org.* iii. 214.
[11] Wroblewsky, *Ann. Chem. Pharm.* clxviii. 200.

According to Hübner and Weiss, it can readily be obtained and in a very pure condition by heating 7 grms. of benzoic acid to 150° with 4 grms. of manganese dioxide which has been washed with hydrochloric acid, and 40 grms. of fuming hydrochloric acid, and re-crystalling the product two or three times.[1]

Properties.—It dissolves at 0° in 2840 parts of water (Kolbe and Lautemann), more readily in hot water and alcohol, and crystallizes in concentrically grouped needles, which melt at 153° and readily sublime. On fusion with caustic potash it yields only metahydroxybenzoic acid[2]; it does not melt under water.

Calcium metachlorobenzoate, $(C_7H_4ClO_2)_2Ca + 3H_2O$, forms scaly crystals, which dissolve in 82·6 parts of water at 12°.

Metachlorobenzoyl chloride, $C_6H_4Cl.COCl$, is a strongly refractive liquid, boiling at 225°.[3]

Metachlorohippuric acid, $C_6H_4Cl.CO.NHCH_2.CO_2H$, is formed together with dichlorohippuric acid by the action of potassium chlorate and hydrochloric acid on hippuric acid,[4] and is found in the urine after metachlorobenzoic acid has been administered.[5] It is a tough, amorphous mass, which is scarcely soluble in cold, more readily in boiling water; it forms crystalline salts. It decomposes into amido-acetic acid and metachlorobenzoic acid when boiled with concentrated hydrochloric acid.

Dichlorohippuric acid, $C_6H_3Cl_2.CO.NH.CH_2.CO_2H$, is less soluble in hot water than the preceding compound, and is converted by long contact with water into a granular crystalline mass; on boiling with hydrochloric acid it decomposes into *a*-dichlorobenzoic acid and amido-acetic acid.

Metachlorobenzonitril, $C_6H_4Cl.CN$, was prepared by Limpricht and Uslar by the distillation of metasulphobenzamide, $C_6H_4(CO.NH_2)SO_2.NH_2$, and metasulphamidobenzoic acid, $C_6H_4(CO_2H)SO_2.NH_2$, with phosphorus chloride. It crystallizes from alcohol in prisms, which smell like benzaldehyde, melt at 40°, and readily volatilize with steam.[1]

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[1] *Ber. Deutsch. Chem. Ges.* vi. 175.
[2] Dembey, *Ann. Chem. Pharm.* cxlviii. 221.
[3] Limpricht and Uslar, *ibid.* cii. 262 ; Graebe ; *ibid.* cxxxviii. 197.
[4] Otto, *ibid.* cxxii. 129.
[5] *Ibid.* cxlii. 346.

Parachlorobenzoic acid, or *Chlorodracylic acid*, was first obtained by Beilstein and Wilbrand from paramidobenzoic acid by the diazo-reaction.[2] Beilstein and Geitner then prepared it by the oxidation of parachlorotoluene with chromic acid solution,[3] while Emmerling found that it is better to employ crude chlorotoluene and a dilute solution of potassium permanganate for this purpose, the orthochlorobenzoic acid formed being easily removed by boiling water.[4] Müller found that it is also formed when chlorobenzene is oxidized with manganese dioxide and sulphuric acid,[5] a formation corresponding to that of benzoic acid from benzene.

Parachlorobenzoic acid dissolves in 5288 parts of water at 10°, crystallizes from alcohol in long, lustrous needles, melts at 236° and sublimes in plates at a higher temperature.

Calcium parachlorobenzöate, $(C_7H_4ClO_2)_2Ca + 3H_2O$, crystallizes in small plates or needles, and is even less soluble in water than the corresponding salt of the meta-acid.

Parachlorobenzoyl chloride, $C_6H_4Cl.COCl$, is a heavy liquid, which fumes in the air, is strongly refractive, and boils at 220°—222° (Emmerling).

Dichlorobenzoic Acids, $C_6H_3Cl_2.CO_2H$.

2125 *a-Dichlorobenzoic acid*, (3 : 4). Otto first prepared this compound by boiling dichlorohippuric acid with hydrochloric acid;[6] it is also obtained by the oxidation of dichlorotoluene and dichlorobenzyl chloride,[7] as well as when parachlorobenzoic acid is heated to 200° with antimony pentachloride.[8]

It is formed, together with the following compound, by heating benzoic acid with bleaching powder solution,[9] or by the action of potassium chlorate and hydrochloric acid,[10] metachlorobenzoic acid being, of course, the first product.

It is slightly soluble in cold, more readily in hot water, and crystallizes in fine, lustrous needles, melting at 201°—202°.

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[1] *Ann. Chem. Pharm.* cvi. 32.

[2] *Ibid.* cxxviii. 270.

[3] *Ibid.* cxxxix. 336.

[4] *Ber. Deutsch. Chem. Ges.* viii. 880.

[5] *Zeitschr. Chem.* 1869, 137.

[6] *Ann. Chem. Pharm.* cxxii. 147.

[7] Beilstein and Kuhlberg, *ibid.* clii. 225 ; Lellmann and Klotz, *ibid.* ccxxxi. 308.

[8] Beilstein, *ibid.* clxxix. 284.

[9] Claus and Thiel, *Ber. Deutsch. Chem. Ges.* viii. 948.

[10] Claus and Pfeifer, *ibid.* v. 658 ; vi. 721.

β-Dichlorobenzoic acid (3:6), is formed by heating orthochlorobenzoic acid with hydrochloric acid and potassium chlorate or potassium dichromate,[1] and by replacing the amido-group of a-chloramidobenzoic acid by chlorine.[2] It crystallizes in needles, which melt at 153·5° (Lellmann and Klotz) and dissolve in about 1200 parts of cold water.

γ-Dichlorobenzoic acid (2:6), is obtained, together with the preceding compounds, when dichlorobenzyl chloride is heated with water to 200°; it crystallizes from alcohol in small needles, melting at 139·5°.[3]

δ-Dichlorobenzoic acid (2:4), is formed by the oxidation of the corresponding dichlorotoluene with nitric acid, and crystallizes in long, pliable needles, melting at 158°.

ε-Dichlorobenzoic acid (3:5), has also been prepared from symmetric dichlorotoluene and forms long needles, melting at 182° (Lellmann and Klotz).

TRICHLOROBENZOIC ACIDS, $C_6H_2Cl_3.CO_2H$.

2126 *α-Trichlorobenzoic acid*, (2:4:6), is obtained by the oxidation of α-trichlorotoluene,[4] and by heating α-trichlorobenzyl chloride[5] to 260° with water; it crystallizes in needles which melt at 163°.

β-Trichlorobenzoic acid has been obtained from the corresponding aldehyde by oxidation with potassium permanganate; it melts at 120°.[6]

γ-Trichlorobenzoic acid, (3:4:5), is formed when chrysanisic acid, $C_6H_2(NO_2)_2(NH_2)CO_2H$, is heated with fuming nitric acid. It forms fine needles, melting at 203°.[7]

TETRACHLOROBENZOIC ACID, $C_6HCl_4.CO_2H$.

Beilstein and Kuhlberg prepared this compound by heating tetrachlorobenzyl chloride with water to 280°; it melts at 187°.

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[1] Beilstein, *Ann. Chem. Pharm.* clxxix. 285.
[2] Rack and Wilkens, *ibid.* ccxxii. 201.
[3] Schultz, *ibid.* clxxxvii. 269.
[4] Jannasch, *ibid.* cxlii. 301
[5] Beilstein and Kuhlberg, *Ber. Deutsch. Chem. Ges.* xviii. 420.
[6] Seelig, *ibid.* xviii. 420.
[7] Salkowski, *Ann. Chem. Pharm.* clxiii. 28.

MONOBROMOBENZOIC ACIDS, $C_6H_4Br.CO_2H$.

2127 *Orthobromobenzoic acid* was first prepared by Griess from anthranilic acid or ortho-amidobenzoic acid by the diazo-reaction, but was not further investigated by him.[1] It was, however, examined by v. Richter, who found it to be identical with that which he had obtained from metabromonitrobenzene by means of the reaction already mentioned (p. 217).[2] Zincke obtained it by boiling orthobromotoluene with dilute nitric acid;[3] it is, however, better to employ a dilute solution of potassium permanganate.[4]

It is more readily soluble in cold water than its isomerides, and is still more soluble in hot water, from which it crystallizes in long needles, which melt at 150° and sublime in small plates.

Barium orthobromobenzoate, $(C_7H_4BrO_2)_2Ba$, is very readily soluble in water, and crystallizes from alcohol in long needles containing two molecules of alcohol.

Metabromobenzoic acid. Peligot obtained this substance in the year 1838 by the action of bromine on silver benzoate,[5] and Herzog, in 1842, by acting upon benzoic acid with bromine in the sunlight.[6] The compound thus prepared, however, was not pure. Reinecke then found that the pure compound can readily be obtained by heating benzoic acid to 100° with bromine and water;[7] it may also be prepared in this manner from benzamide, the reaction taking place at 120°,[8] and bromanil being formed at the same time:

$$C_6H_5.CO.NH_2 + Br_2 + H_2O = C_6H_4Br.CO_2H + NH_4Br.$$

According to Hübner and Angerstein, it can also be prepared by Peligot's method, if dry silver benzoate be submitted to the action of bromine vapour in the sunlight.[9] Griess also obtained it from metamidobenzoic acid[10] and Sandmeyer from metabromaniline, which he diazotized and brought into a solution of potassium cuprous bromide heated to 90°; the nitril, which was thus formed, was then decomposed by boiling soda-solution;[1] Wroblewsky prepared it by the oxidation of metabromotoluene.[2]

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[1] *Ann. Chem. Pharm.* cxxxv. 121.

[2] *Ber. Deutsch. Chem. Ges.* iv. 464; v. 428.

[3] *Ibid.* vii. 1502.

[4] Rhalis, *Ann. Chem. Pharm.* cxcviii. 102.

[5] *Ibid.* xxviii. 246.

[6] Brandes, *Arch. Pharm.* xxiii. 16.

[7] *Zeitschr. Chem.* 1865, 116; 1869, 100.

[8] Friedberg, *Ann. Chem. Pharm.* clviii. 26.

[9] *Ibid.* clviii. 2.

[10] *Ibid.* cxvii. 25.

Metabromobenzoic acid is very slightly soluble in water, readily in alcohol, crystallizes in needles, melts at 155°, sublimes at a higher temperature and boils above 280°. On fusion with caustic potash, metahydroxybenzoic acid is formed together with a little salicylic acid, and, probably, some parahydroxybenzoic acid.

Barium metabromobenzoate, $(C_7H_4BrO_2)_2Ba + 4H_2O$, is very slightly soluble in water and crystallizes in small, flat needles.

Parabromobenzoic acid was first obtained by Griess from paramidobenzoic acid.[3] It is formed by the oxidation of parabromotoluene,[4] parabromo-ethylbenzene,[5] etc., with dilute nitric acid or chromic acid, and may also be obtained from parabromaniline by means of Weith's reaction (Part III. p. 31).[6] It is almost insoluble in cold water, and only slightly soluble in boiling water, from which it crystallizes in small plates. It is readily soluble in alcohol and ether, and separates from them in small needles, melting at 251°.

Barium parabromobenzoate, $(C_7H_4BrO_2)_2Ba$, crystallizes in nacreous plates, which are readily soluble in water.

DIBROMOBENZOIC ACIDS, $C_6H_3Br_2CO_2H$.

	Br. : Br.		Melting-point.
α)	3 : 4	small needles,[7]	229°—230°
β)	2 : 3	small needles,[8]	147°
γ)	3 : 5	flat needles,[9]	213°—214°
δ)	2 : 5	flat needles,[10]	153°
ε)	2 : 4	needles or tablets,[11] . . .	168°—170°

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[1] *Ber. Deutsch. Chem. Ges.* xviii. 1495.

[2] *Ann. Chem. Pharm.* clxviii. 156.

[3] *Ibid.* cxxxv. 121.

[4] Hübner, Ohly and Philipp, *ibid.* cxliii. 247.

[5] Fittig and König, *ibid.* cxliv. 283.

[6] Weith and Landolt, *Ber. Deutsch. Chem. Ges.* viii. 717.

[7] Burghardt and Beutnagel, *Ann. Chem. Pharm.* ccxxii. 184.

[8] Beutnagel, *ibid.* ccxxii. 105.

[9] Beilstein and Geitner, *ibid.* cxxxix. 4; Neville and Winther, *Ber. Deutsch. Chem. Ges.* xiii. 970.

[10] Holzapfel, *Ann. Chem. Pharm.* ccxxii. 107.

[11] Neville and Winther, *loc. cit.*

Tribromobenzoic Acids, $C_6H_2Br_3.CO_2H$.

	Melting-point.
a) silky needles[1]	234°—235°
β) small needles[2]	195°
γ) needles[3]	186·5°
δ) needles[4]	178°

Pentabromobenzoic acid, $C_6Br_5.CO_2H$. When metabromobenzoic acid is heated to 150° with bromine and water, *a*-tribromobenzoic acid is formed, and on further heating with bromine at 200° is converted into pentabromobenzoic acid. It crystallizes from alcohol in thin plates or long, broad needles which become brown and melt at 234°—235° (Reinecke).

Mono-iodobenzoic Acids, $C_6H_4I.CO_2H$.

2128 *Ortho-iodobenzoic acid* was obtained by Griess and Richter from anthranilic acid, and by the latter also from meta-iodonitrobenzene. Kekulé prepared it by the oxidation of ortho-iodotoluene with dilute nitric acid. It is slightly soluble in water, readily in alcohol, and crystallizes in long, white needles, which melt at 157° and readily sublime. On fusion with potash, salicylic acid is formed.

Meta-iodobenzoic acid has been prepared by Griess, Lunge, and Hübner, and by Grothe from metamidobenzoic acid. It is also formed when benzoic acid is heated with potassium iodate and dilute sulphuric acid, and by the action of iodine and iodic acid on sodium benzoate. It forms small plates or needles, melting at 186°—187°; on heating with caustic potash solution it is converted into metahydroxybenzoic acid, and with ammonia into metamidobenzoic acid.

Para-iodobenzoic acid was obtained by Griess[5] from paramidobenzoic acid, and by Körner[6] by the oxidation of para-iodotoluene. It crystallizes in small plates melting at 256°.[7]

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[1] Reinecke, *Zeitschr. Chem.* 1869, 110.

[2] Smith, *Ber. Deutsch. Chem. Ges.* x. 1706.

[3] Vollbrecht, *ibid.* x. 1708.

[4] Lawrie, *ibid.* x. 1705.

[5] *Ber. Deutsch. Chem. Ges.* iv. 522.

[6] *Zeitschr. Chem.* 1868, 327.

[7] Schmidt and Schultz, *Ann. Chem. Pharm.* ccvii. 333.

According to Beran it cannot be obtained perfectly pure by recrystallization, but must be sublimed, plates which melt at 265°—266°[1] being obtained in this way.

MONOFLUORBENZOIC ACIDS, $C_6H_4F.CO_2H$.

2129 These compounds are obtained by passing nitrogen trioxide into solutions of the amidobenzoic acids in alcohol, a diazo-amidobenzoic acid being formed, which is decomposed into fluorbenzoic acid and amidobenzoic acid hydrofluoride on warming with fuming hydrofluoric acid:[2]

$$\begin{array}{l} N.C_6H_4.CO_2H \\ \| \\ N.NH.C_6H_4.CO_2H \end{array} + HF = C_6H_4F.CO_2H + NH_2.C_6H_4.CO_2H + N_2.$$

They can be still more simply obtained from the diazobenzoic acid sulphates (p. 260).

As much as 5 grms. of these compounds may be administered daily to a dog without injuring it; they appear in the urine as the fluorhippuric acids,[3] $C_9H_8FNO_3$, which crystallize in needles or prisms.

Orthofluorbenzoic acid crystallizes in fine needles, is readily soluble in alcohol, more readily in water, and melts at 117°—118°.

Orthofluorhippuric acid melts at 121·5°.

Metafluorbenzoic acid crystallizes from hot water in broad, lustrous plates or needles, which resemble those of benzoic acid and melt at 123°—124°.

Metafluorhippuric acid melts at 152°—153°.

Parafluorbenzoic acid resembles the meta-compound, and melts at 180°—181°. This substance was first prepared by Schmitt and v. Gehren from ordinary amidobenzoic acid, and was therefore looked upon as metafluorbenzoic acid. The amido-acid employed probably contained the para-compound as an impurity. The fluorbenzoic acid crystallizes, according to their account, in pointed rhombic prisms, which have a characteristic sweet taste, and melt at 182°. On distillation with lime it yields phenol, which was mistaken by Schmitt and v. Gehren for fluorbenzene; a high boiling compound is also formed, which probably consists chiefly of diphenyl oxide:[1]

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[1] *Ber. Deutsch. Chem. Ges.* xviii. 137.

[2] Schmitt and v. Gehren, *Journ. Prakt. Chem.* [2] i. 394 ; Paternò and Oliveri, *Gaz. Chim.* 1882, 95.

[3] Coppola, *ibid.* xiii. 121

$$(C_6H_4F.CO_2)_2Ca + 2Ca(OH)_2 = 2C_6H_5.OH + CaF_2 + 2CaCO_3.$$

Parafluorhippuric acid melts at 161·5°.

Difluorbenzoic acid, $C_6H_3F_2.CO_2H$, is formed, together with chromic fluoride, when benzoic acid is treated with chromium hexfluoride. It is scarcely soluble in cold, only slightly in boiling water, but more readily in hot benzene, and sublimes less readily than benzoic acid, in flat, white needles, melting at 232°.

Calcium difluorbenzoate, $(C_6H_3F_2.CO_2)_2Ca + 3H_2O$, crystallizes from hot water in fascicular aggregates of white, lustrous needles, which dissolve in 200 parts of water at 15°.[2]

NITRO-SUBSTITUTION PRODUCTS OF BENZOIC ACID.

2130 In the year 1839, Plantamour obtained an acid very rich in oxygen by the action of nitric acid on cinnamic acid, benzaldehyde being also formed. He gave no name to the new substance, since he wished to ascertain by investigation whether it could be classed along with any known acid. Analysis led to the formula $C_{13}H_{10}O_9$, and this formula was confirmed by the composition of the silver salt.[3]

In the next year, Mulder found that *nitrobenzinic acid* is formed by the action of nitric acid on benzoic acid, cinnamic acid and oil of cinnamon. He determined the correct composition of the compound and formulated it as $C_{14}H_8O_4 + N_2O_3 + H_2O$, according to which it is a compound of nitrous acid with an organic substance containing two atoms of hydrogen less, and one atom of oxygen more than benzoic acid. He also found it to be identical with the acid discovered by Plantamour, who had overlooked the presence of nitrogen.[4]

The same acid was prepared by Blyth and Hofmann by the distillation of styrolene (phenylethylene) with strong nitric acid.[5]

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[1] Paternò and Oliveri, *Gaz. Chim.* xiii. 533.

[2] Jackson and Hartshorn, *Ber. Deutsch. Chem. Ges.* xviii. 1993.

[3] *Ann. Chem. Pharm.* xxx. 348.

[4] *Ibid.* xxxiv. 297.

[5] *Ibid.* liii. 304.

Abel detected it among the products of the action of nitric acid on cumene (isopropylbenzene),[1] and Blumenau obtained it in the same way from dragon's blood.[2] The acid formed by the nitration of benzoic acid was then investigated by Zinin,[3] Gerland,[4] Voit[5] and Ernst,[6] the three last-mentioned giving directions for its preparation.

Glénard and Boudault had, in 1843, obtained nitrodracylic acid, $C_8H_6(NO_2)O_2$, by the action of fuming nitric acid on the dracyl (toluene) obtained from dragon's blood, and Gerhardt considered it to be nitrobenzoic acid.[7] Wilbrand and Beilstein showed, however, that it is not identical, but isomeric with the latter, and that another acid is formed in small quantity, which appears to be ordinary nitrobenzoic acid.[8] It was obtained about the same time by Fischer, who named it paranitrobenzoic acid,[9] while that derived from benzoic acid was known as orthonitrobenzoic acid until it was recognized as belonging to the meta-series (Part III., p. 41).

The third isomeride, now known as orthonitrobenzoic acid, was first prepared by Radziswesky from phenylacetic acid, but was believed to be ordinary nitrobenzoic acid.[10] Beilstein and Kuhlberg then prepared the ortho-acid from cinnamic acid (phenylacrylic acid),[11] and considered it as identical with Radziswesky's compound, this being confirmed by Pirogow.[12]

Griess was the first to recognize the fact that not only metanitrobenzoic acid, but also its two isomerides are formed by the nitration of benzoic acid; from 4,000 grms. of benzoic acid he obtained, in addition to the chief product, 347 grms. of orthonitrobenzoic acid and 35 grms. of paranitrobenzoic acid,[13] while according to Widnmann, the ortho-acid formed amounts to 25 per cent. of the weight of benzoic acid employed.[14] The older investigators had all the three nitrobenzoic acids under their observation, but their purest compounds were probably specimens in which one or other of the isomerides simply predominated. This is shown by the following facts; toluene, cumene, styrolene, oil of cinnamon and cinnamic acid are oxidized by dilute nitric acid to benzoic acid, which is converted by the concentrated acid into the nitrobenzoic acids. Toluene is converted by strong nitric acid into the three isomeric nitrotoluenes, the chief product being the para-compound, the meta-compound being only formed in small quantity (p. 15), while on the nitration of benzoic acid, the meta-acid forms the chief product, and the para-compound only occurs in small quantity. Concentrated nitric acid converts cinnamic acid, and probably styrolene and cumene, into para- and ortho-nitro-compounds, the meta-compound being possibly formed in small quantity. All these nitro-derivatives of the hydrocarbons, as well as the nitro-cinnamic acids, yield the corresponding nitrobenzoic acids on oxidation.

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[1] *Ann. Chem. Pharm.* lxiii. 308.

[2] *Ibid.* lxvii. 313.

[3] *Journ. Prakt. Chem.* xxxvi. 93.

[4] *Ann. Chem. Pharm.* lxxxvi. 143; xci. 185.

[5] *Ibid.* xcix. 100.

[6] *Zeitschr. Chem.* 1860, 477.

[7] *Ann. Chem. Pharm.* xlviii. 343.

[8] *Ibid.* cxxvi. 255; cxxviii. 257.

[9] Fischer, *ibid.* cxxvii. 137.

[10] *Ber. Deutsch. Chem. Ges.* iii. 648.

[11] *Ann. Chem. Pharm.* clxiii. 121.

[12] *Ibid.* clxiii. 140.

[13] *Ibid.* clxvi. 129; *Ber. Deutsch. Chem. Ges.* x. 1868.

[14] *Ann. Chem. Pharm.* cxcliii. 223.

Which of these predominated, therefore, in the mixtures in question, depended, in the first instance, upon the concentration of the nitric acid employed. The nitrobenzoic acid obtained from cinnamic acid and styrolene was probably a mixture of the para- and ortho-acids, and this would also be the composition of that obtained from dragon's blood and cumene by the aid of fuming nitric acid. These mixtures may, however, have also contained dinitrobenzoic acids and styphnic acid, both of which are formed by the action of nitric acid on benzoic acid.

MONONITROBENZOIC ACIDS, $C_6H_4(NO_2)CO_2H$.

2131 *Orthonitrobenzoic acid.* In order to prepare this compound, the mixture obtained by the nitration of benzoic acid is converted into the barium salts, from which the barium orthonitrobenzoate can readily be obtained in crystals, which are then decomposed by dilute sulphuric acid.[1]

Orthonitrobenzoic acid can also be readily obtained by boiling orthonitrotoluene for a long time with a solution of potassium permanganate.[2] Crude nitrotoluene may also be employed since the larger portion of the slightly soluble paranitrobenzoic acid can easily be separated. The barium salts are prepared from the mother-liquors of this and separated as described below.[3]

Orthonitrobenzoic acid dissolves in 100 parts of water at 16·5°; it is more readily soluble in hot water and crystallizes from it in large colourless needles. It is obtained in asymmetric tablets or prisms by the spontaneous evaporation of its alcoholic solution. It melts at 147°, and has an intensely sweet taste, which also characterizes its salts.

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[1] Widnmann, *Ann. Chem. Pharm.* cxciii. 202.
[2] Widnmann, *Ber. Deutsch. Chem. Ges.* viii. 392.
[3] Monnet, Reverdin and Nölting, *ibid.* xii. 443.

Barium orthonitrobenzoate, $(C_6H_4.NO_2.CO_2)_2Ba + 3H_2O$, crystallizes on the spontaneous evaporation of its solution in water, in which it is more readily soluble than the acid, in large, yellow, asymmetric tablets, which lose their water over sulphuric acid.

Ethyl orthonitrobenzoate, $C_6H_4(NO_2)CO_2.C_2H_5$, forms asymmetric crystals, melting at 30°.

Orthonitrobenzoyl chloride, $C_6H_4(NO_2)COCl$, is a faint yellow liquid, which solidifies at a low temperature to a crystalline mass, and decomposes on heating. When heated with silver cyanide, the nitril of nitrophenylglyoxylic acid is formed, and this is converted by reduction into isatin, an oxidation product of indigo.[1]

Orthonitrobenzonitril, $C_6H_4(NO_2)CN$. By the action of ammonia on orthonitrobenzoyl chloride, orthonitrobenzamide, $C_6H_4(NO_2)CO.NH_2$, is formed, and crystallizes in long needles, melting at 174°; it is converted into the nitril on heating with phosphorus pentoxide.[2] The latter may also be obtained synthetically from orthonitraniline by diazotizing it with hydrochloric acid and sodium nitrite, and bringing the compound thus obtained into an almost boiling solution of copper sulphate and potassium cyanide:[3]

$$2C_6H_4(NO_2)N_2Cl + Cu_2(CN)_2 = 2C_6H_4(NO_2)CN + N_2 + Cu_2Cl_2.$$

It crystallizes in needles which are readily soluble in alcohol and hot water, melt at 109°, and sublime when more strongly heated.

2132 *Metanitrobenzoic acid* is best obtained by bringing an intimate mixture of one part of previously fused and finely powdered benzoic acid with two parts of nitre into three or four parts of sulphuric acid, the mixture being well stirred, and then heating until the nitrobenzoic acids have separated out as an oily layer.[4] In a well-conducted operation these contain little or no unaltered benzoic acid. Should this be present in large quantity, it is removed by distillation with water, and the product then heated to boiling with 20 parts of water and neutralized with barium hydroxide. Barium metanitrobenzoate crystallizes out on cooling. The mother liquor is evaporated and the residue repeatedly extracted with small quantities of cold water, the salt of the ortho-acid being obtained on the evaporation of the solution. A further crop of crystals of the meta-compound are obtained by dissolving the residue in 20 parts of boiling water and cooling the solution, the barium salts of paranitrobenzoic acid, benzoic acid and styphnic acid remaining in solution.

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[1] Claissen and Shadwell, *Ber. Deutsch. Chem. Ges.* xii. 350.

[2] Bärthlein, *ibid.* x. 1713.

[3] Sandmeyer, *ibid.* xviii. 1492.

[4] Ernst, *loc. cit.*; Leo Liebermann, *Ber. Deutsch. Chem. Ges.* x. 862; Widnmann, *Ann. Chem. Pharm.* cxciii. 216.

Metanitrobenzoic acid dissolves at 16·5° in 425, and at 100° in 10 parts of water; on cooling it separates from the solution in small plates; it crystallizes from dilute alcohol in monoclinic tablets, melting at 140°—141°; when gradually cooled the melting-point falls to 135°—136°, but rises again after some time, or when the remelted acid is allowed to cool rapidly (Widnmann). It possesses the characteristic property of melting under hot water; it commences to sublime at temperatures above 100°, and its vapour provokes coughing.

Sodium metanitrobenzoate, $C_6H_4(NO_2)CO_2Na + 3H_2O$, crystallizes in coarse, colourless or yellowish tablets, and may be employed for the purification of the crude acid.[1]

Barium metanitrobenzoate, $(C_6H_4.NO_2.CO_2)_2Ba + 4H_2O$, crystallizes in thin prisms, and is less soluble than the free acid.

Ethyl metanitrobenzoate, $C_6H_4(NO_2)CO_2.C_2H_5$, has been prepared by the action of hydrochloric acid on an alcoholic solution of the acid, by that of alcohol on its chloride, and by the nitration of ethyl benzoate. It is also formed when ethyl nitrate and benzoic acid in ethereal solution are treated with sulphuric acid.[2] It crystallizes in monoclinic prisms, which melt at 41° and have an aromatic smell, boils at 298°, and decomposes into ethylene bromide and metanitrobenzoic acid when heated to 170°—200° with bromine.[3]

Metanitrobenzoyl chloride, $C_6H_4(NO_2)COCl$, crystallizes in pyramids with a diamond lustre or in long, fine prisms, which melt at 33°—34°[4] and smell like benzoyl chloride.

Metanitrobenzamide, $C_6H_4(NO_2)CO.NH_2$, forms yellow, monoclinic needles, and melts at 140°—142°.

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[1] Hübner, *Ann. Chem. Pharm.* ccxxii. 72.
[2] Fittica, *Journ. Prakt. Chem.* [2] xvii. 221.
[3] Naumann, *Ann. Chem. Pharm.* cxxxiii. 202.
[4] Claissen and Thompson, *Ber. Deutsch. Chem. Ges.* xii. 1943.

[illegible] acid, [illegible]. Ber-[illegible] obtained this compound in the year 185[illegible] by taking 6 grms. of [illegible] acid and [illegible] separating the [illegible] acid from [illegible]. It is also prepared [illegible] by adding sulphuric acid [illegible] solution of hippuric acid in cold fuming nitric acid. It crystallizes from alcohol in silky needles melting at 162°. It is decomposed by boiling fuming hydrochloric acid into glycocoll and nitrobenzoic acid.[1]

[illegible], [illegible], is formed by the action of [illegible] on the amide, as well as by the [illegible] and, [illegible], from [illegible] in a similar manner to the [illegible]-compound. It crystallizes in needles melting at [illegible].[2]

[illegible] acid is prepared by the oxidation of paranitrotoluene with strong nitric acid Beilstein and Wilbrand; [illegible] with potassium dichromate and dilute sulphuric acid[3] or with potassium permanganate.[4]

It dissolves in [illegible] parts of water at [illegible], and in 140 parts at 100° without melting, is more readily soluble in alcohol and crystallizes in yellowish white lustrous plates, which melt at 238° and sublime in needles.

Barium paranitrobenzoate, $(C_6H_4NO_2CO_2)_2Ba + 5H_2O$, crystallizes in yellow transparent monoclinic prisms, which dissolve in 25[illegible] parts of cold and [illegible] parts of boiling water. It forms an anhydrous double salt with barium benzoate, $(C_6H_5CO_2)_2Ba + (C_6H_4NO_2CO_2)_2Ba$, which crystallizes in large, colourless or brownish lenticular aggregates. The calcium salt and calcium *metanitrobenzoate* both form double salts with calcium benzoate.[5]

Ethyl paranitrobenzoate, $C_6H_4(NO_2)CO_2C_2H_5$, forms assymetric plates, which melt at 57°, and are converted by heating with ammonia into *paranitrobenzamide*, $C_6H_4(NO_2)CO.NH_2$, which crystallizes in needles melting at 197°—198°.

Paranitrobenzoyl chloride, $C_6H_4(NO_2)COCl$, boils at 202°—205° under a pressure of 105 mm., and crystallizes from petroleum spirit in fine needles, melting at 75°.[6]

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[1] *Ann. Chem. Pharm.* lxxviii. 100; Schwanert, *ibid.* cxii. 69; Conrad. *Journ. Prakt. Chem.* [2] xv. 254.

[2] Beilstein, *Ann. Chem. Pharm.* cxlvi. 336; Engler, *ibid.* cxlix. 297: Schöppf, *Ber. Deutsch. Chem. Ges.* xviii. 1063.

[3] Beilstein and Geitner, *Ann. Chem. Pharm.* cxxxix. 335; Körner, *Zeitschr. Chem.* 1869, 635; Rosenstiehl, *ibid.* 1869, 701.

[4] Michael and Norton, *Ber. Deutsch. Chem. Ges.* x. 580.

[5] Salkowsky, *ibid.* ix. 24; x. 1257.

[6] Gevekoht, *Ann. Chem. Pharm.* ccxxi. 335.

Paranitrobenzonitril, $C_6H_4(NO_2)CN$, is obtained by heating the amide with phosphorus pentoxide,[1] as well as by diazotizing paranitraniline and pouring the solution into a well agitated solution of potassium cuprous cyanide in potassium cyanide, heated to 90°.[2] It crystallizes from alcohol in plates, and sublimes on heating in long, feathery crystals, melting at 147°.

Paranitrohippuric acid, $C_6H_4(NO_2)CO.NH.CH_2.CO_2H$, is formed, together with paranitrobenzoic acid, by the passage of paranitrotoluene through the system in the dog, and is found in the urine combined with urea. It crystallizes from hot water in orange-red prisms, melting at 129°.[3]

So-called isomerides of the three nitrobenzoic acids. It was early stated by Mills that four mononitrobenzoic acids exist, and Fittica thought that he had prepared five new isomerides, differing from the three already mentioned in their melting points, three of them being also distinguished by their citron-yellow colour. He obtained these substances "by peculiar methods, which chiefly consisted in avoiding with the greatest care all trustworthy modes of purification," [4] but the researches of others have shown that his compounds do not exist.[5] The melting points and physical properties of the nitrobenzoic acids, like those of benzoic acid itself, are greatly altered by very small quantities of admixed impurities; when benzoic acid is nitrated, small amounts of the dinitrobenzoic acids are always formed in addition to the three mononitrobenzoic acids, and the product also contains benzoic acid and styphnic acid (trinitroresorcinol), the latter of which gives it its yellow colour.

Bodewig found that three of Fittica's new acids are simply impure forms of metanitrobenzoic acid, which he obtained from them by crystallization; the two others gave no measurable crystals; he also observed that this acid, besides its stable form, exists in two unstable modifications, which also crystallize in the monoclinic system, but differ from the stable form in their crystallographic constants. Their crystals soon become opaque, from the formation of the stable form, a change which takes place in one of the unstable modifications even when its crystals are allowed to remain in the mother liquor. He further

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[1] Fricke, *Ber. Deutsch. Chem. Ges.* vii. 1322.

[2] Sandmeyer, *ibid.* xviii. 1492.

[3] Jaffé, *ibid.* vii. 1673.

[4] Kekulé, *Lehrb. Org. Chem.* iii. 554.

[5] Erlenmeyer and Widnmann, *Ber. Deutsch. Chem. Ges.* viii. 392; Griess, *ibid.* viii. 526; Ladenburg, *ibid.* viii. 535 and 853; Salkowsky, *ibid.* viii. 636; Liebermann, *ibid.* x. 1036; Claus, *ibid.* xiii. 891; Fittica, *ibid.* xiii. 1537.

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proved their identity by converting them into the ethyl ether.[1] Fittica's [illegible] derivatives have no more real existence than [illegible] acid (p. [illegible]).

DINITROBENZOIC ACIDS, $C_6H_3(NO_2)_2CO_2H$.

[illegible] The appended numbers indicate the position of the nitroxyls when that of the carboxyl is 1.

α-Dinitrobenzoic acid (2 : 5), was obtained by Griess, together with the two following and another acid, by heating one part of metanitrobenzoic acid with ten parts of a mixture of equal volumes of fuming sulphuric and nitric acids.[2] It is slightly soluble in cold water, and on evaporation separates out in prisms; it is deposited from the hot saturated solution as a yellowish oil, which solidifies in needles melting at 177°. It is reduced to α-diamidobenzoic acid by tin and hydrochloric acid.

Barium α-dinitrobenzoate, $(C_6H_3(NO_2)_2CO_2)_2Ba + 4H_2O$, forms long, six-sided plates, which are slightly soluble in cold, more readily in hot water.

β-Dinitrobenzoic acid (2 : 4), is also formed by the oxidation of ordinary dinitrotoluene with fuming nitric acid,[3] and by the nitration of paranitrobenzoic acid.[4] It melts in hot water and crystallizes from it in long, lustrous, brittle needles, or on spontaneous evaporation in large, rhombic tablets or prisms, which melt at 179° and have a bitter taste. Tin and hydrochloric acid convert it into metadiamidobenzene, carbon dioxide being eliminated.

Barium β-dinitrobenzoate, $(C_6H_3(NO_2)_2CO_2)_2Ba + 3H_2O$, is tolerably soluble in cold water and crystallizes in white, rhombic, or six-sided tablets.

γ-Dinitrobenzoic acid, (2 : 6), is very freely soluble in boiling water, crystallizes in fine, matted, white needles, melts at 202°, and, like its isomerides, has a very bitter taste. It decomposes on distillation into carbon dioxide and metadinitrobenzene, and on reduction yields metadiamidobenzene.

Barium γ-dinitrobenzoate, $(C_6H_3(NO_2)_2CO_2)_2Ba + 2H_2O$, is very readily soluble in water and crystallizes in needles.

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[1] *Ber. Deutsch. Chem. Ges.* xii. 1983; *Zeitschr. Kryst.* iv. 58.
[2] *Ber. Deutsch. Chem. Ges.* vii. 1223.
[3] Tiemann and Judson, *ibid.* iii. 223; Wurster, *ibid.* vii. 148.
[4] Claus and Halberstadt, *ibid.* xiii. 815; Stromeyer, *Ann. Chem. Pharm.* cxxxii. 79.

δ-Dinitrobenzoic acid, (3 : 5), or *Ordinary dinitrobenzoic acid*, was first prepared by Cahours:[1] it is obtained by heating benzoic acid[2] or metanitrobenzoic acid[3] with a mixture of nitric and sulphuric acids, or by oxidizing symmetric dinitrotoluene with chromic acid[4] or nitric acid (Hübner).

In order to prepare it, 20 grms. of benzoic acid are dissolved in 180 grms. of concentrated sulphuric acid, one-third of the volume of fuming nitric acid added, and the whole heated nearly to boiling for four hours and then poured into two volumes of cold water; a yield of 30 grms is obtained.[5]

It crystallizes from hot water in thin, quadratic tablets, and from alcohol in prisms, which melt at 204°—205°, and sublime in needles. On reduction it yields δ-diamidobenzoic acid. Its salts detonate violently when heated.

Barium δ-dinitrobenzoate, $(C_6H_3(NO_2)_2CO_2)_2Ba+H_2O$, forms small crystals, readily soluble in hot water (Hübner).

ε-Dinitrobenzoic acid, (3 : 4), is formed at the same time as the β-acid by the action of a mixture of nitric and sulphuric acids on paranitrobenzoic acid. It has an intensely bitter taste, is only slightly soluble in cold water, fuses under hot water and crystallizes from it in stellate groups, melting at 161°. These crystals sublime at a higher temperature, and detonate violently when heated on platinum foil.[6]

Barium ε-dinitrobenzoate, $(C_6H_3(NO_2)_2CO_2)_2Ba+4H_2O$, forms a white, radiating crystalline mass.

TRINITROBENZOIC ACID, $C_6H_2(NO_2)_3CO_2H$.

2135 This compound is obtained by heating trinitrotoluene to 100° with fuming nitric acid for a week. It crystallizes from hot water in rhombic prisms, melts at 190° and sublimes at a higher temperature.[7]

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[1] *Ann. Chem. Pharm.* lxix. 241.
[2] Michler, *ibid.* clxxv. 152.
[3] Muretow, *Zeitschr. Chem.* 1870, 641.
[4] Städel, *Ber. Deutsch. Chem. Ges.* xiv. 902.
[5] Hübner, *Ann. Chem. Pharm.* ccxxii. 72.
[6] Claus and Halberstadt, *Ann. Chem. Pharm.* xiii. 815.
[7] Tiemann and Judson, *ibid.* iii. 224.

CHLORONITROBENZOIC ACIDS, $C_6H_3Cl(NO_2)CO_2H$.

	$Cl : NO_2$		Melting-point.
α	2 : 5	silky needles or rhombic tablets[1] . .	164°—165°
β	3 : 6	prisms[2]	137°—138°
γ	3 : 2	long, thin needles or six-sided tablets[3]	235°
δ	3 : 5	small needles[4]	147°
ε	4 : 3	small needles[5]	179°—180°
ζ	2 : 4	readily soluble crystals[6]	136°—137°

The first three of these acids have been obtained by the nitration of ortho- and meta-chlorobenzoic acid. The fourth acid is prepared from the corresponding amidonitrobenzoic acid and the fifth by the nitration of parachlorobenzoic acid; this compound and the last have also been obtained by the oxidation of the corresponding chloronitrotoluenes. Since the ζ-acid melts at the same temperature as the β-acid, they were considered to be identical, but this is not the case, as the ζ-acid is derived from paranitrotoluene, and can be converted into orthochlorobenzoic acid.

BROMONITROBENZOIC ACIDS, $C_6H_3Br(NO_2)CO_2H$.

	$Br : NO_2$		Melting-point
α)	2 : 5	long needles[7]	177°—178°
β)	3 6	monoclinic prisms[8]	140°—140°
γ)	3 : 2	monoclinic crystals[9]	250°
δ)	4 : 3	small plates or needles[10]	199°
ε)	3 : 5	long needles or thin, six-sided tablets[11]	161°
ζ)	2 : 4	long needles[12]	163°—164°

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[1] Kekulé, *Ann. Chem. Pharm.* cxvii. 135; Hübner, *Zeitschr. Chem.* 1886, 614; Hübner and Biedermann, *Ann. Chem. Pharm.* cxlvii. 263; Wilkens and Rack, *ibid.* ccxxii. 192.

[2] Ulrich, *ibid* ccxxii. 95.

[3] *Ibid.*

[4] Grube, *Ber. Deutsch. Chem. Ges.* x. 1703.

[5] Hübner and Biedermann; Raveill, *Ann. Chem. Pharm.* ccxxii. 182.

[6] Wachendorff, *ibid.* clxxxv. 275

[7] Burghard, *Ber. Deutsch. Chem. Ges.* viii. 560; Rahlis, *Ann. Chem. Pharm.* cxcviii. 109; Scheufelen, *ibid.* ccxxxi. 181.

[8] Hübner, Ohly and Philipp, *ibid.* cxliii. 233; Hübner and Mecker, *Zeitschr. Chem.* 1867, 565; Hübner and Petermann, *Ann. Chem. Pharm.* cxlix. 132; ccxxii. 101.

[9] *Ibid.*

[10] *Ibid.*; Raveill, *Ber. Deutsch. Chem. Ges.* x. 1707; *Ann. Chem. Pharm.* ccxxii. 177; Scheufelen.

[11] Hesemann and Köhler, *ibid.* ccxxii. 166.

[12] Scheufelen.

The first is formed by the nitration of orthobromobenzoic acid, as well as by the oxidation of the corresponding bromonitrotoluene, and yields δ-dibromobenzoic acid when the nitroxyl is replaced by bromine. The following two have been prepared from metabromobenzoic acid and are converted into anthranilic acid by reduction (Part III., p. 50). The δ-acid is obtained from parabromobenzoic acid and from metanitrobromotoluene, the ε-acid from the corresponding amidonitrobenzoic acid, and the ζ-acid by the oxidation of the corresponding bromonitrotoluene.

Iodonitrobenzoic Acids, $C_6H_3I(NO_2)CO_2H$.

	$I : NO_2$		Melting-point
α)	3 : 2	slightly soluble crystals[1]	235°
β)	3 : 6	readily soluble, melts under water[2] . . .	179°
γ)	3 : 4	readily soluble, does not melt under water[3]	192°
δ)	4 : 3	readily soluble in alcohol, very slightly in water[4]	210°

The first three are formed by the nitration of meta-iodobenzoic acid, and the last one from para-iodobenzoic acid.

MONAMIDOBENZOIC ACIDS, $C_6H_4(NH_2)CO_2H$.

2136 *Ortho-amidobenzoic acid.* Fritzsche, in his research on aniline, mentioned that the product of the first action of potash on indigo is a characteristic acid, which he subsequently obtained pure by employing indigo-blue in the place of crude indigo. He determined its composition, and his results were confirmed by the remarkable decomposition which occurred on heating. "Anthranilic acid decomposes when it is heated to a temperature just exceeding its melting-point into carbon dioxide, which is given off as a gas, and aniline."[5]

Liebig looked upon this research as of exceptional interest, and its confirmation appeared to him to be so important and necessary that he instituted further investigations, which corroborated the results obtained by Fritzsche.[1] At the same time he discovered an excellent method for the preparation of anthranilic acid which will be described below.

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[1] Cunze and Hübner, *ibid.* cxxxv. 106; Grothe, *Journ. Prakt. Chem.* [2] xviii. 324.

[2] *Ibid.*

[3] *Ibid.*

[4] Glassner, *Ber. Deutsch. Chem. Ges.* viii. 562.

[5] *Journ. Prakt. Chem.* xxiii. 67; *Ann. Chem. Pharm.* xxxix. 76.

Gerland subsequently showed that the acid in question is isomeric with benzamic acid (metamidobenzoic acid).[2] Hübner and Petermann succeeded in preparing anthranilic acid synthetically from benzoic acid by the nitration of metabromobenzoic acid; they obtained two isomeric nitrobromobenzoic acids, $C_6H_3Br(NO_2)CO_2H$, both of which yielded anthranilic acid on reduction (Part III. p. 51). It may be more simply obtained by the reduction of orthonitrobenzoic acid with tin and hydrochloric acid;[3] the tin is precipitated with sulphuretted hydrogen and the filtrate evaporated to dryness, the residue treated with an excess of ammonia and the solution then acidified with acetic acid. The greater portion of the anthranilic acid crystallizes out; the remainder is then obtained as the copper salt by the method described below.

Sandmeyer observed that almost half of the nitrobenzoic acid is converted into salicylic acid on reduction with tin and hydrochloric acid.[4]

In order to prepare it from indigo the crude material is finely powdered and boiled for two hours with ten times its amount of strong caustic potash solution, a small quantity of manganese dioxide being occasionally added and the original volume of the solution maintained throughout the operation by the repeated addition of small quantities of water. The solution is then neutralized with sulphuric acid, freed from most of the potassium sulphate by crystallization and evaporated to dryness. Potassium anthranilate is extracted from the residue by alcohol and is then converted into the copper salt, which is obtained as a light green precipitate by distilling off the alcohol, acidifying with acetic acid and adding copper acetate or sulphate; the free acid is obtained from this by the action of sulphuretted hydrogen.[5] Böttinger found that the only definite compound formed in this reaction, in addition to 28 per cent. of anthranilic acid, is formic acid:[6]

$$C_{16}H_{10}N_2O_2 + 2O + 4H_2O = 2C_7H_7NO_2 + 2CH_2O_2.$$

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[1] *Ann. Chem. Pharm.* xxxix. 91. [2] *Ibid.* lxxxvi. 143.

[3] Beilstein and Kuhlberg, *Ann. Chem. Pharm.* clxiii. 138.

[4] *Ber. Deutsch. Chem. Ges.* xviii. 1494.

[5] Hübner and Petermann, *Ann. Chem. Pharm.* cxlix. 142

[6] *Ber. Deutsch. Chem. Ges.* x. 269.

Ortho-amidobenzoic acid dissolves in about 250 parts of cold, more readily in hot water, and readily in alcohol. The solution has a sweet taste, but is acid to litmus paper, and shows a blue fluorescence when the acid is pure. It crystallizes in small plates, or on the gradual evaporation of its solution, in rhombic needles, melts at 145°, and sublimes when carefully heated, but decomposes into carbon dioxide and aniline when distilled, more completely when mixed with powdered glass (Liebig). On treatment with sodium amalgam, benzoic acid and ammonia are formed (Hübner and Petermann):

$$C_6H_4(NH_2)CO_2H + 2H = C_6H_5.CO_2H + NH_3.$$

Most of its metallic salts crystallize well.

Ortho-amidobenzoic acid hydrochloride, $C_7H_7NO_2.HCl$, is readily soluble in water and alcohol, slightly in ether, and crystallizes in needles or four-sided prisms, melting at 191°; its solution is not precipitated by platinum chloride.

Formortho-amidobenzoic acid, $2C_6H_4(NH.CHO)CO_2H + H_2O$, is obtained by heating ortho-amidobenzoic acid with formic acid, and crystallizes from chloroform in fine, matted needles, which, after drying, form a light, very readily electrified mass, and melt at 168°. When it is heated with phosphorus pentoxide, phenyl carbamine is formed.[1]

Acetortho-amidobenzoic acid, $C_6H_4(NH.C_2H_3O)CO_2H$, is formed by the oxidation of acetorthotoluide with potassium permanganate,[2] and by heating a mixture of equal molecules of anthranilic acid and acetic anhydride.[3] It is slightly soluble in cold, readily in hot water, and crystallizes from acetic acid in flat, rhombic needles, which melt at 179°—180°.

Diacetortho-amidobenzoic acid, $C_6H_4N(C_2H_3O)_2CO_2H$, is obtained by boiling anthranilic acid with an excess of acetic anhydride, and forms crystals, melting at 220° (Bedson and King).

Benzortho-amidobenzoic acid, $C_6H_4(NH.CO.C_6H_5)CO_2H$, is formed by the action of benzoyl chloride on anthranilic acid and by the oxidation of benzoylorthotoluide. It crystallizes from alcohol in long needles, melting at 182°.[4]

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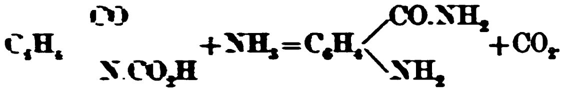
[1] v. Meyer and Bellmann, *Journ. Prakt. Chem.* [2] xxxiii. 24.

[2] Bedson and King, *Ber. Deutsch. Chem. Ges.* xiv. 263.

[3] Jackson, *ibid.* xiv. 886.

[4] Brückner, *Ann. Chem. Pharm.* ccv. 134.

Ortho-amidobenzamide, $C_6H_4(NH_2)CO.NH_2$, is formed when anthranilcarboxylic acid is dissolved in aqueous ammonia:



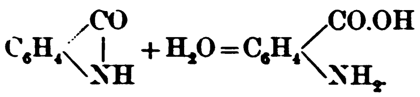
$$C_6H_4\begin{cases}CO\\ N.CO_2H\end{cases} + NH_3 = C_6H_4\begin{cases}CO.NH_2\\ NH_2\end{cases} + CO_2.$$

It crystallizes from hot water in nacreous plates, and from chloroform in large, white plates, melts at 108°, and boils with slight decomposition at about 300°. It is converted into ortho-amidobenzoic acid by acids and alkalis.[1]

Ortho-amidobenzonitril, $C_6H_4(NH_2)CN$, is obtained by the action of tin and hydrochloric acid on orthonitrobenzonitril; it crystallizes in yellowish needles, melts at 103°, and forms readily soluble salts.[2]

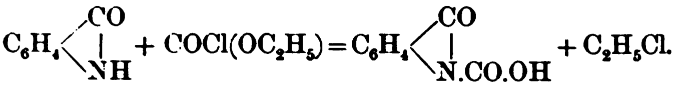
2137 *Anthranil*, C_7H_5NO, is formed by the action of tin on a solution of orthonitrobenzaldehyde in glacial acetic acid, and is a colourless, oily liquid, which has a characteristic, penetrating smell, is volatile with steam, and commences to boil at 210°—215°, the greater portion of it being decomposed. It rapidly becomes brown and resinous when exposed to the air or to light. It is a very feeble base, and combines with mercuric chloride to form the compound $C_7H_5NO + HgCl_2$, which crystallizes in fine needles and is readily soluble in alcohol and hot water, but on heating with a solution of potassium chloride, is resolved into its constituents.[3]

Anthranil is converted into anthranilic acid by the action of alkalis:



$$C_6H_4\begin{cases}CO\\ |\\ NH\end{cases} + H_2O = C_6H_4\begin{cases}CO.OH\\ NH_2.\end{cases}$$

When heated with ammonia and ferrous sulphate it is converted into orthonitrobenzaldehyde, while *anthranilcarboxylic acid* is formed when it is heated with ethyl chlorocarbonate:



$$C_6H_4\begin{cases}CO\\ |\\ NH\end{cases} + COCl(OC_2H_5) = C_6H_4\begin{cases}CO\\ |\\ N.CO.OH\end{cases} + C_2H_5Cl.$$

This compound crystallizes from hot water in fine needles, which decompose into carbon dioxide and anthranil at 230°. It olves in dilute caustic soda, forming a solution which possesses plendid blue fluorescence; this, however, soon disappears, hranilic acid being formed. Anthranilcarboxylic acid is also ained by the oxidation of isatin, and will be more fully cribed along with this substance.

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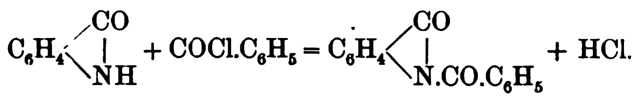
[1] Kolbe, *Journ. Prakt. Chem.* [2] xxx. 475.
[2] Bärthlein, *Ber. Deutsch. Chem. Ges.* x. 1713.
[3] Friedländer and Henriques, *ibid.* xv. 2105.

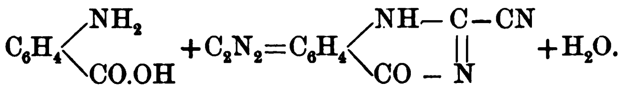
Benzoylanthranil is readily obtained by the action of benzoyl oride on anthranil:



$$C_6H_4\left\langle\begin{array}{l}CO\\ |\\ NH\end{array}\right. + COCl.C_6H_5 = C_6H_4\left\langle\begin{array}{l}CO\\ |\\ N.CO.C_6H_5\end{array}\right. + HCl.$$

crystallizes from a mixture of benzene and ligroïn in long dles, which melt at 122°—123°, and dissolve when heated h dilute alkalis, benzortho-amidobenzoic acid being formed.[1]

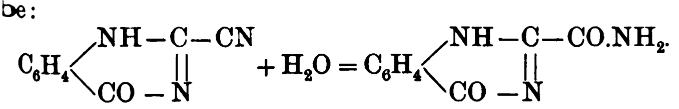
Dicyanamidobenzoyl, $C_9H_5N_3O$, is the name given by Griess to ompound which he obtained by passing cyanogen into a cold eous solution of anthranilic acid:



$$C_6H_4\left\langle\begin{array}{l}NH_2\\ CO.OH\end{array}\right. + C_2N_2 = C_6H_4\left\langle\begin{array}{l}NH-C-CN\\ \quad\ \ \ \ \|\\ CO\ -\ N\end{array}\right. + H_2O.$$

is slightly soluble in water, readily in hot alcohol, and stallizes in small, yellowish prisms; although it does not tain a carboxyl group, it has an acid reaction and is a nobasic acid.[2]

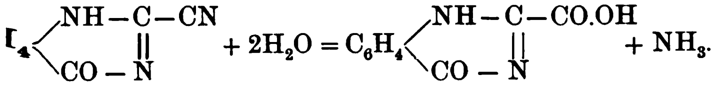
Carboxamidocyanamidobenzoyl, $C_9H_7N_3O_2$, is formed when the ceding compound is heated with strong ammonia in a sealed be:



$$C_6H_4\left\langle\begin{array}{l}NH-C-CN\\ \quad\ \ \ \ \|\\ CO\ -\ N\end{array}\right. + H_2O = C_6H_4\left\langle\begin{array}{l}NH-C-CO.NH_2.\\ \quad\ \ \ \ \|\\ CO\ -N\end{array}\right.$$

crystallizes from hot water in fine needles and from alcohol in tes, has an acid reaction and forms salts with bases, the hydrogen the imido-group being probably replaced by the metal.

arboxylcyanamidobenzoyl, $2C_9H_6N_2O_3+H_2O$, is obtained by ting dicyanamidobenzoyl with baryta water:



$$_4\left\langle\begin{array}{l}NH-C-CN\\ \quad\ \ \ \ \|\\ CO\ -\ N\end{array}\right. + 2H_2O = C_6H_4\left\langle\begin{array}{l}NH-C-CO.OH\\ \quad\ \ \ \ \|\\ CO\ -\ N\end{array}\right. + NH_3.$$

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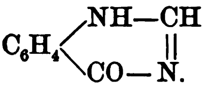
[1] Friedländer and Wleügel, *Ber. Deutsch. Chem. Ges.* xvi. 2227.

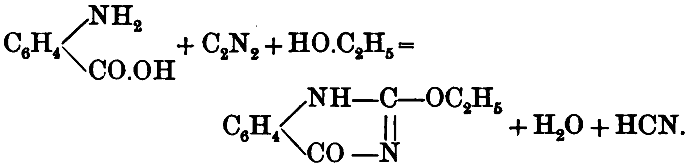
[2] *Ibid.* xi. 1986 and 2180.

It crystallizes in small, white plates, which are slightly soluble in cold water and alcohol; it is a dibasic acid. When it is boiled with water or acids, or simply heated, carbon dioxide is evolved and *carbimidamidobenzoyl*, $C_8H_6N_2O_2$, formed. This compound crystallizes from hot water in needles melting at 214°. It possesses basic properties and has the following constitution:



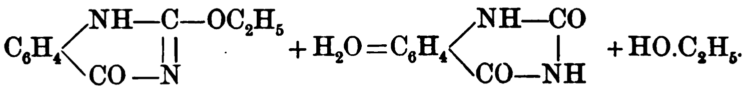
Griess has also prepared various other derivatives of dicyanamidobenzoyl.[1]

Ethoxycyanamidobenzoyl, $C_{10}H_{10}N_2O_2$, is formed when an alcoholic solution of anthranilic acid is saturated with cyanogen, allowed to stand for some time and then evaporated:



It crystallizes from hot alcohol in needles, melts at 173°, and can be distilled in small quantities without undergoing decomposition.[2]

2138 *Uramidobenzoyl*, $C_8H_6N_2O_2$, is prepared by fusing anthranilic acid with urea or by boiling the preceding compound with hydrochloric acid:



It is slightly soluble in water and alcohol, crystallizes in lustrous plates melting above 350°, dissolves in caustic potash solution and is reprecipitated by carbon dioxide. Fuming nitric acid converts it into *nitro-uramidobenzoyl*, $C_8H_5(NO_2)N_2O_2$, which crystallizes in honey-yellow prisms, and is converted by reduction into the slightly soluble *amido-uramidobenzoyl*, $C_8H_5(NH_2)N_2O_2$, which forms yellow needles and yields salts, which are also only slightly soluble and crystallize well (Griess).

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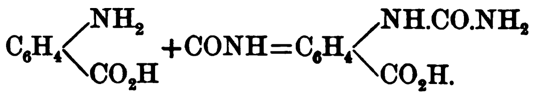
[1] *Ber. Deutsch. Chem. Ges.* xviii. 2417.

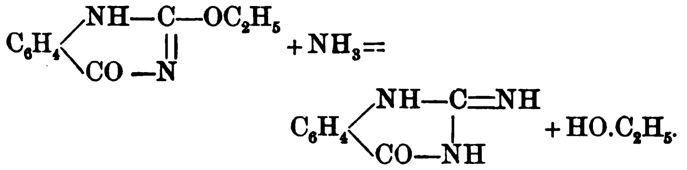
[2] Griess, *ibid.* ii. 415.

Ortho-uramidobenzoic acid, $C_8H_8N_2O_3$. This compound, which is the acid corresponding to the anhydride just described, is formed by the action of potassium cyanate on ortho-amidobenzoic acid hydrochloride:[1]

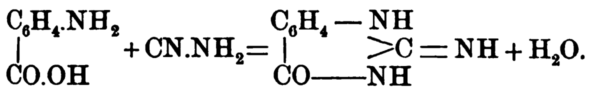


It crystallizes in needles, and on treatment with nitric acid only yields one dinitro-compound, which will be subsequently mentioned.

Orthobenzoglycocyamidine, or *Benzoylguanidine*, $C_8H_7N_3O$, is obtained by heating ethoxycyanamidobenzoyl with alcoholic ammonia:



It may also be obtained by allowing a solution containing cyanamide and anthranilic acid to stand:[2]



$$\begin{array}{l} C_6H_4.NH_2 \\ | \\ CO.OH \end{array} + CN.NH_2 = \begin{array}{l} C_6H_4 - NH \\ | \qquad\quad >C = NH \\ CO - NH \end{array} + H_2O.$$

It crystallizes in nacreous plates, which are only slightly soluble in water and alcohol.

Benzoylguanidine nitrate, $C_8H_8N_3O.NO_3$, is a very characteristic salt; it crystallizes in small plates, which are almost insoluble in water and alcohol.

2139 *a-Methylorthobenzoglycocyamidine*, or *a-Orthobenzocreatinine*, $C_8H_6(CH_3)N_3O$, is formed when a strongly alkaline solution of the preceding compound is treated with methyl iodide and allowed to stand for some days. It is almost insoluble in cold, slightly soluble in hot water, more readily in boiling alcohol, and

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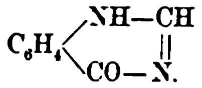
[1] Griess, *Journ. Prakt. Chem.* [2] v. 371.

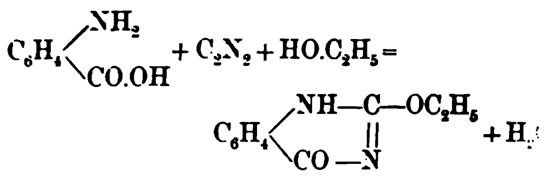
[2] Griess, *Ber. Deutsch. Chem. Ges.* xiii. 977.

It crystallizes in small, white plates, which are slightly in cold water and alcohol; it is a dibasic acid. When it is with water or acids, or simply heated, carbon dioxide is e and *carbimidamidobenzoyl*, $C_5H_6N_2O_2$, formed. This com crystallizes from hot water in needles melting at 21 possesses basic properties and has the following constitutio



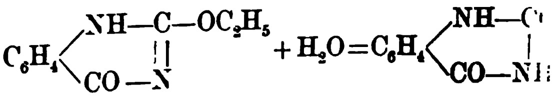
Griess has also prepared various other derivatives of amidobenzoyl.[1]

Ethoxycyanamidobenzoyl, $C_{10}H_{10}N_2O_2$, is formed v alcoholic solution of anthranilic acid is saturated with allowed to stand for some time and then evaporated:



It crystallizes from hot alcohol in needles, melts can be distilled in small quantities withou decomposition.[2]

2138 *Uramidobenzoyl*, $C_8H_6N_2O_2$, is prepar anthranilic acid with urea or by boiling the pound with hydrochloric acid:



It is slightly soluble in water and alcohol, crystalli plates melting above 350°, dissolves in caustic p and is reprecipitated by carbon dioxide. Fum converts it into *nitro-uramidobenzoyl*, $C_8H_5(NO$ crystallizes in honey-yellow prisms, and is into the slightly soluble *amid*

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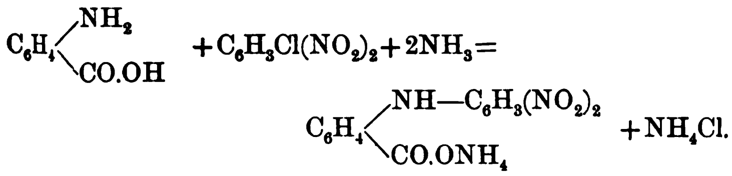
[1] *Ber. Deu*

[2] Griess,

Oxalanthranilic acid is slightly soluble in cold water, readily in alcohol and ether, and crystallizes from the latter in hard needles united to form druses. It is a powerful dibasic acid.

Normal calcium benzamoxalate, $2C_9H_5NO_5Ca + 5H_2O$, is the most characteristic salt of this acid. It separates out in glittering prisms when calcium chloride is added to a solution of the ammonium salt.

2140 *Dinitrodiphenylamine-orthocarboxylic acid*, $C_6H_4(NH.C_6H_3(NO_2)_2)CO_2H$, is formed when anthranilic acid is heated with chlorodinitrobenzene, ($Cl:NO_2:NO_2 = 1:2:4$), and an excess of ammonia:

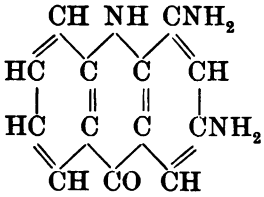


$$C_6H_4\begin{cases}NH_2\\CO.OH\end{cases} + C_6H_3Cl(NO_2)_2 + 2NH_3 = C_6H_4\begin{cases}NH—C_6H_3(NO_2)_2\\CO.ONH_4\end{cases} + NH_4Cl.$$

The ammonium salt produced in this way forms lustrous, ruby-red plates; the free acid is obtained by the addition of strong hydrochloric acid to this salt, and is almost insoluble in water, only very slightly soluble in cold alcohol and glacial acetic acid, crystallizing from a hot mixture of these in small, orange-yellow, matted needles, which fuse at 262°—264° to a brownish red liquid, which appears almost black when seen in thick layers; when it is carefully heated a portion distils without decomposition, but it detonates when rapidly heated on platinum foil.

Its alkaline salts are slightly soluble in cold, more readily in hot water, and crystallize in reddish yellow to ruby-red plates, which detonate on heating. All the other salts are almost insoluble. The barium salt is a dark cinnabar-red precipitate.

This compound does not yield the corresponding amido-acid on reduction with tin and hydrochloric acid, but this is converted into *diamidohydro-acridine ketone* with elimination of water; this substance, which will be subsequently described, has the following constitution:



Other amido-acids, in which the carboxyl does not stand in the ortho-position to the amido-group, also yield dinitrodiphenylaminecarboxylic acids with chlorodinitrobenzene, but these are converted by reduction into the corresponding diamido-acids.

This reaction, therefore, may be employed as a ready method for ascertaining whether or not an aromatic amido-acid belongs to the ortho-series. The compound to be tested is heated to boiling with chlorodinitrobenzene, alcohol and some ammonia for some time. If an ortho-compound be present, the product yields on reduction a base insoluble in alkalis; in other cases an acid is obtained.[1]

2141 *Metamidobenzoic acid.* Zinin obtained this compound in 1845 by the action of ammonium sulphide on nitrobenzinic acid (metanitrobenzoic acid) and named it *benzamic acid.*[2] Chancel, in 1849, converted nitrobenzamide into amidobenzamide by the same method, but he looked upon the substance obtained as aniline urea and named it *carbanilamide.* By boiling it with caustic potash solution he obtained *carbanilidic acid,* which Gerland subsequently proved to be identical with benzamic acid.[3] Voit, who investigated its salts, remarked that the latter name is unsuitable, since only the radicals of dibasic acids form amic-acids, and he therefore proposed the name amidobenzoic acid.[4]

In order to prepare it, a solution of metanitrobenzoic acid in strong ammonia is saturated with sulphuretted hydrogen in absence of air, concentrated and treated with acetic acid. Metanitrobenzoic acid may also be reduced with tin and hydrochloric acid and the double tin salt of the amido-acid decomposed with sulphuretted hydrogen. The amidobenzoic acid is then precipitated from the filtrate, previously neutralized with ammonia, by acetic acid.

It is slightly soluble in cold, more readily in hot water and alcohol, and crystallizes in warty masses of needles, which melt at 174° and partially volatilize at a higher temperature without decomposition; when it is heated with spongy platinum (Chancel) or baryta, it decomposes into carbon dioxide and aniline. Its solution has an acid reaction but a sweet taste, and decomposes in the air with separation of a brown powder, its alkaline solution behaving in a similar manner. Its metallic salts crystallize well.

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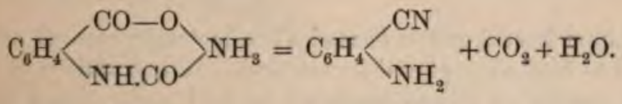
[1] Jourdan, *Ber. Deutsch. Chem. Ges.* xviii. 1444.
[2] *Journ. Prakt. Chem.* xxxvi. 93.
[3] *Ann. Chem. Pharm.* lxxxvi. 142.
[4] *Ibid.* xcix. 100.

Metamidobenzoic acid hydrochloride, $C_7H_7NO_2.ClH$, crystallizes in prisms, which are readily soluble in water, slightly in hydrochloric acid; the platinichloride forms golden-yellow needles, and the double tin salt, $C_7H_7NO_2.ClH+SnCl_2$, crystallizes in plates (Beilstein and Wilbrand). Its other compounds with acids also crystallize well.

Metamidobenzamide, $C_6H_4(NH_2)CO.NH_2$, is obtained, according to Chancel, when ammonium sulphide is added to a boiling aqueous solution of metanitrobenzamide. It is readily soluble in water, and forms large, yellow crystals, melting at 75°.[1] Like amidobenzoic acid it is a monacid base.

Metamidobenzonitril, $C_6H_4(NH_2)CN$, is formed when metanitrobenzonitril is reduced with zinc and hydrochloric acid[2] or tin and acetic acid,[3] as well as by heating meta-uramidobenzoic acid with phosphoric acid:[4]



$$C_6H_4\left<\begin{array}{l}CO-O\\NH.CO\end{array}\right>NH_3 = C_6H_4\left<\begin{array}{l}CN\\NH_2\end{array}\right. + CO_2 + H_2O.$$

It crystallizes from dilute alcohol in long, white needles, melts at 53°—54°, boils at 288°—290°, and is decomposed by powerful reducing agents into ammonia and benzonitril, the latter being partially converted into benzylamine. When it is treated with alcoholic potash and chloroform, the carbamine, $C_6H_4(NC)CN$, is formed; it has an overpowering odour and has not been further investigated. Metamidobenzonitril is a monacid base and forms salts which crystallize well.

Methylmetamidobenzoic acid, or *Metabenzosarcosine*, $C_6H_4(NH.CH_3)CO_2H$, was obtained by Griess as a decomposition product of α-benzocreatine; it is slightly soluble in cold, more readily in hot water, and crystallizes in small plates.

Dimethylmetamidobenzoic acid, $C_6H_4.N(CH_3)_2CO_2H$. The methyl ether of this acid is formed by a molecular change from the following compound, and is a liquid which has a faint aromatic odour, and boils at 270°. The acid is obtained from it by decomposition with alcoholic potash, and is also only slightly soluble in hot water; it crystallizes in dull needles, melting at 151°.

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[1] Beilstein and Reichenbach, *Ann. Chem. Pharm.* cxxxii. 142.

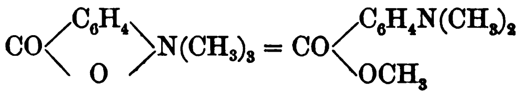
[2] Hofmann, *Ber. Deutsch. Chem. Ges.* i. 196.

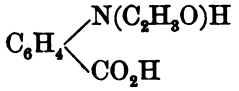
[3] Fricke, *ibid.* vii. 1321.

[4] Griess, *ibid.* viii. 861.

Trimethylamidobenzoic acid, or *Metabenzobetaïne*, $C_7H_4N(CH_3)_3O_2 + H_2O$. The iodide of this compound is formed when a solution of amidobenzoic acid in methyl alcohol is allowed to stand in contact with an excess of caustic potash and methyl iodide; it forms short prisms of the formula $C_7H_5O_2N(CH_3)_3I + H_2O$. The free base, which is obtained by the action of lead hydroxide, crystallizes in deliquescent needles, which lose one molecule of water at 105°, and have a neutral reaction and bitter taste.

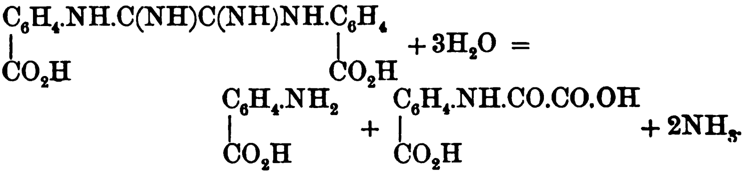
The anhydrous compound is converted on fusion into the methyl ether of the preceding compound.[1]





Acetmetamidobenzoic acid, $C_6H_4\begin{cases}N(C_2H_3O)H\\CO_2H\end{cases}$, is metameric with hippuric acid and is formed when metamidobenzoic acid is heated to 160° with glacial acetic acid. It crystallizes in fine, white needles, is almost insoluble in cold water, has a bitter taste, at the same time resembling that of saltpetre, and melts at 245°; it sublimes, however, at a lower temperature.[2]

2142 *Amidobenzoic acid percyanide*, $(C_6H_4(NH_2)CO_2H)_2C_2N_2$, is the name given by Griess to a compound to which he had previously assigned the formula $C_6H_4(NH_2)CO_2HC_2N_2$, and which is obtained by passing cyanogen into an aqueous solution of metamidobenzoic acid. It is a yellow, crystalline substance, which is insoluble in water, scarcely soluble in alcohol and ether, and has acid properties. On distillation it decomposes into water, carbon dioxide, ammonia, ammonium cyanide and metamidobenzonitril. When heated to 130° with alcohol, it decomposes into metamidobenzoic acid and metabenzamoxalic acid.



$$\underset{CO_2H}{C_6H_4}.NH.C(NH)C(NH)NH.\underset{CO_2H}{C_6H_4} + 3H_2O = \underset{CO_2H}{C_6H_4}.NH_2 + \underset{CO_2H}{C_6H_4}.NH.CO.CO.OH + 2NH_3.$$

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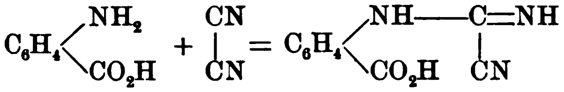
[1] Griess, *Ber. Deutsch. Chem. Ges.* vi. 586.

[2] Forster, *Ann. Chem. Pharm.* cxvii. 165; Kaiser, *Ber. Deutsch. Chem. Ges.* xviii. 2946.

Metabenzamoxalic acid, or *Oxalamidobenzoic acid,* is also formed by heating metamidobenzoic acid with oxalic acid, and crystallizes from hot water in narrow white plates.[1]

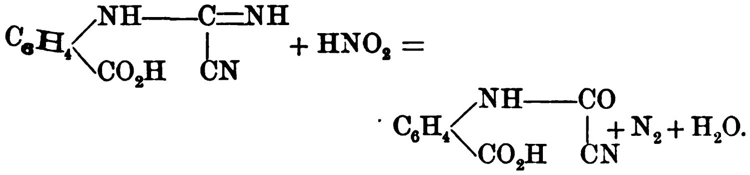
Cyanocarbimidobenzoic acid, $3C_9H_7N_3O_2 + H_2O$, is formed together with the percyanide according to the equation :



$$C_6H_4\begin{cases}NH_2\\CO_2H\end{cases} + \begin{matrix}CN\\|\\CN\end{matrix} = C_6H_4\begin{cases}NH\text{——}C{=}NH\\CO_2H\quad\ \ |\\ \qquad\quad\ \ CN\end{cases}$$

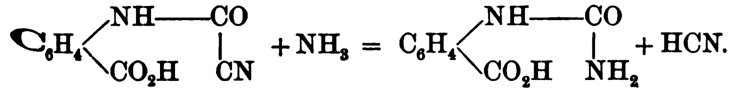
It is only very slightly soluble in cold water, readily in hot alcohol, and crystallizes in elliptical plates, which have an acid reaction and combine with bases and acids.

Cyanocarboxamidobenzoic acid, $C_9H_6NO_3$, is obtained by the action of nitrous acid on a cold solution of the preceding compound in hydrochloric acid :



$$C_6H_4\begin{cases}NH\text{——}C{=}NH\\CO_2H\quad\ \ |\\ \qquad\quad\ \ CN\end{cases} + HNO_2 = C_6H_4\begin{cases}NH\text{——}CO\\CO_2H\quad\ \ |\\ \qquad\quad\ \ CN\end{cases} + N_2 + H_2O.$$

It crystallizes in lustrous, white plates, which have a sweet taste, and are almost insoluble in cold water, but are decomposed by boiling water with formation of carbon dioxide, hydrocyanic acid and carboxamidobenzoic acid. When it is dissolved in ammonia, uramidobenzoic acid is formed :



$$C_6H_4\begin{cases}NH\text{——}CO\\CO_2H\quad\ \ |\\ \qquad\quad\ \ CN\end{cases} + NH_3 = C_6H_4\begin{cases}NH\text{——}CO\\CO_2H\quad\ \ |\\ \qquad\quad\ \ NH_2\end{cases} + HCN.$$

Methylamine, ethylamine, &c., act in a similar manner, and a large number of substituted uramidobenzoic acids can, therefore, be prepared in this way.[2]

If cyanogen be passed into an alcoholic solution of metamidobenzoic acid, the percyanide, which has been already mentioned, is deposited, and the two following compounds crystallize out on allowing the mother liquor to stand:

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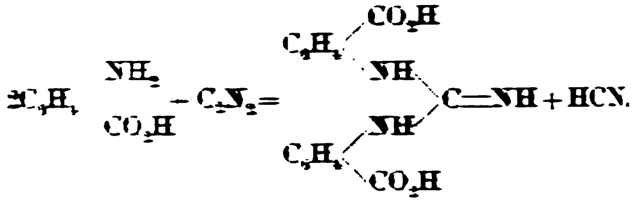
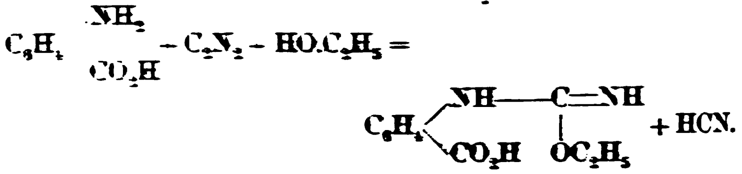
[1] Griess, *Ber. Deutsch. Chem. Ges.* i. 191 ; xi. 1985 ; xvi. 336 ; xviii. 2412 ; Schiff, *ibid.* xix. 252.

[2] Griess, *ibid.* xviii. 2415.

Carbimidamidobenzoic acid.



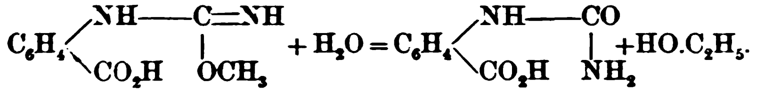
Ethoxycarbimidamidobenzoic acid.



Carbimidamidobenzoic acid, or *Guanidodibenzoic acid*, $C_{15}H_{13}N_3O_4$, is obtained from the crude product by extraction with boiling water: it separates out on cooling in needles, which are purified by being dissolved in hydrochloric acid, the solution neutralized with ammonia and then precipitated by acetic acid. The precipitate is at first amorphous, but soon changes into needles. It forms salts with both acids and bases.[1]

Ethoxycarbimidamidobenzoic acid, $2C_{10}H_{12}N_2O_3 + 3H_2O$, is slightly soluble in water, more readily in alcohol, and crystallizes in needles.[2]

Meta-uramidobenzoic acid, $C_8H_8N_2O_3 + H_2O$, is formed when the preceding compound is boiled with hydrochloric acid:



Menschutkin obtained it from potassium cyanate and metamidobenzoic acid hydrochloride, and named it *oxybenzuramic acid*.[3] Griess then showed that it is also formed by bringing metamidobenzoic acid into fused urea.[4] It is slightly soluble in water, more readily in alcohol, and crystallizes in needles or fine prisms. Its salts have been investigated by Menschutkin. On treatment with concentrated nitric acid it yields three dinitro-compounds (p. 255).

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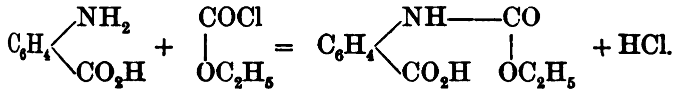
[1] Griess, *Zeitschr. Chem.* 1867, 534.
[2] *Journ. Prakt. Chem.* [2] iv. 296.
[3] *Ann. Chem. Pharm.* cliii. 84.
[4] *Ber. Deutsch. Chem. Ges.* ii. 47.

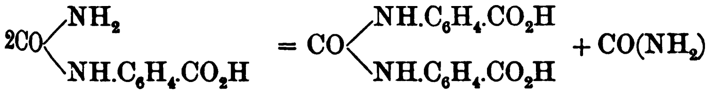
Meta-urethanebenzoic acid, $C_{10}H_{11}NO_4$, is formed by the action of nitrous acid on ethoxycarbimidamidobenzoic acid[1] and by treating metamidobenzoic acid with ethyl chlorocarbonate:



$$C_6H_4\Big\langle\begin{array}{l}NH_2\\CO_2H\end{array} + \begin{array}{l}COCl\\|\\OC_2H_5\end{array} = C_6H_4\Big\langle\begin{array}{ll}NH— & CO\\ & |\\CO_2H & OC_2H_5\end{array} + HCl.$$

It crystallizes in plates, which are slightly soluble in water, dissolve in alcohol in every proportion, and melt at 189°.

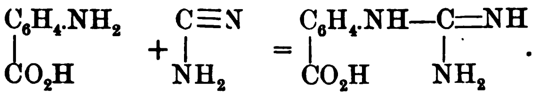
Carboxamidobenzoic acid, or *Metacarbamidobenzoic acid*, $C_{15}H_{12}N_2O_5$, is obtained by heating uramidobenzoic acid to 200°, or by repeatedly evaporating the solution of its barium salt:[2]



$$2CO\Big\langle\begin{array}{l}NH_2\\NH.C_6H_4.CO_2H\end{array} = CO\Big\langle\begin{array}{l}NH.C_6H_4.CO_2H\\NH.C_6H_4.CO_2H\end{array} + CO(NH_2)_2.$$

It is also formed when meta-urethanebenzoic acid is heated above its melting-point,[3] and crystallizes in microscopic needles, which are insoluble in water, alcohol and ether.

2143 *Metabenzoglycocyamine*, or *Metaguanidobenzoic acid*, $C_8H_9N_3O_2 + H_2O$, was first obtained by Griess by boiling amidobenzoic acid percyanide with caustic potash solution; it is also formed by the action of ammonia on ethoxycarbimidamidobenzoic acid, as well as, similarly to glycocyamine (Part II. p. 97), by allowing an alcoholic and ammoniacal solution of cyanamide and metamidobenzoic acid to stand:[4]



$$\begin{array}{l}C_6H_4.NH_2\\|\\CO_2H\end{array} + \begin{array}{l}C\equiv N\\|\\NH_2\end{array} = \begin{array}{ll}C_6H_4.NH— & C{=}NH\\| & |\\CO_2H & NH_2\end{array}.$$

It is slightly soluble in alcohol, and crystallizes from hot water in thin, four-sided tablets which dissolve in caustic potash, but are reprecipitated by carbon dioxide. It forms salts with the mineral acids, but does not combine with acetic acid. On boiling with baryta water, uramidobenzoic acid is first formed:

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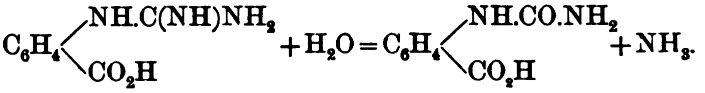
[1] Griess, *Ber. Deutsch. Chem. Ges.* ix. 796.

[2] Griess, *Zeitschr. Chem.* 1868, 650; *Ann. Chem. Pharm.* clxxii. 170.

[3] Wachendorff, *Ber. Deutsch. Chem. Ges.* xi. 701.

[4] Griess, *ibid.* vii. 575; viii. 323.



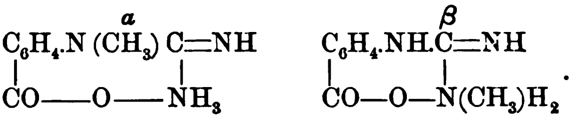
$$C_6H_4\left\langle\begin{matrix}NH.C(NH)NH_2\\CO_2H\end{matrix}\right. + H_2O = C_6H_4\left\langle\begin{matrix}NH.CO.NH_2\\CO_2H\end{matrix}\right. + NH_3.$$

On continued boiling, metamidobenzoic acid and urea or decomposition products of these are produced.

a-Metabenzocreatine, $2C_8H_8(CH_3)N_3O_2+3H_2O$, is formed by the action of methyl iodide and caustic potash on a solution of the preceding compound. It is slightly soluble in water and alcohol, crystallizes in pointed plates, and decomposes into urea and benzosarcosine when boiled with baryta water.

β-Metabenzocreatine is prepared from ethoxycarbimidamidobenzoic acid and methylamine, and crystallizes from hot water in small plates. On heating with baryta water it yields metaamidobenzoic acid, methylamine, and carbon dioxide (Griess).

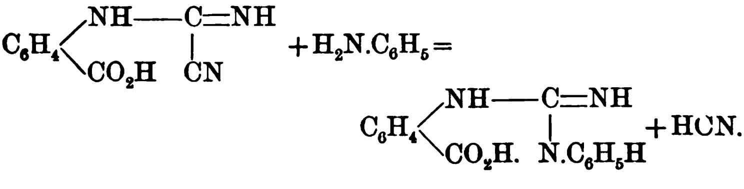
The metabenzocreatines, like benzoglycocyamine, exist in the free state as salts, and have the following constitution:



$$\begin{array}{c}a\\ \begin{array}{lll}C_6H_4.N\,(CH_3) & C{=}NH & \\ | & | & \\ CO\text{——}O\text{——} & NH_3 & \end{array}\end{array}\qquad \begin{array}{c}\beta\\ \begin{array}{ll}C_6H_4.NH. & C{=}NH\\ | & |\\ CO\text{—}O\text{—} & N(CH_3)H_2\end{array}\end{array}.$$

If these compounds be compared with those of the ortho-series, it is found that the latter contain a molecule of water less or are anhydro-compounds, this class of bodies being very readily formed by and characteristic of the ortho-series.

Phenylmetabenzoglycocyamine, $C_8H_8(C_6H_5)N_3O_2+H_2O$, is formed when cyanocarbimidamidobenzoic acid is heated with aniline:



$$C_6H_4\left\langle\begin{matrix}NH\text{——}C{=}NH\\ CO_2H\quad\;\; \overset{|}{C}N\end{matrix}\right. + H_2N.C_6H_5 = C_6H_4\left\langle\begin{matrix}NH\text{——}C{=}NH\\ CO_2H.\quad \overset{|}{N}.C_6H_5H\end{matrix}\right. + HCN.$$

It is insoluble in alcohol, but slightly soluble in hot water, readily in hydrochloric acid and caustic potash, and crystallizes in needles or plates, which have a bitter taste followed by a sweet after-taste.

Amidophenylmetabenzoglycocyamine, $C_8H_8(C_6H_4.NH_2)N_3O_2$, is prepared in a similar manner from paradiamidobenzene; it crystallizes in small prisms, and is a diacid base.[1]

2144 *Paramidobenzoic acid* is obtained by the reduction of paranitrobenzoic acid with ammonium sulphide,[2] or better with tin and hydrochloric acid.[3] It is tolerably soluble in water, very readily in alcohol, and crystallizes in long needles forming fascicular aggregates; it melts at 186°—187°, and decomposes at a higher temperature into carbon dioxide and aniline, a decomposition which may also be effected by heating it to 160°—180° with hydrochloric acid.

It is characteristic of paramidobenzoic acid that lead acetate gives with its aqueous solution a crystalline precipitate of the double salt, $C_7H_4(NH_2)O_2PbC_2H_3O_2$.[4]

Paramidobenzoic acid hydrochloride, $C_7H_7NO_2.HCl$, crystallizes in small plates or prisms.

Paramidobenzamide, $C_6H_4(NH_2)CO.NH_2$, is formed by the reduction of paranitrobenzamide with ammonium sulphide, and forms large, light yellow crystals, which melt at 178°—179°, and are much less soluble in water than those of the meta-compound.[5]

Paramidobenzonitril, $C_6H_4(NH_2)CN$, may be prepared from paranitrobenzonitril,[6] and by the distillation of para-uramidobenzoic acid with phosphorus pentoxide.[7] It is readily soluble in alcohol and boiling water, and crystallizes in needles, melting at 100° (Fricke). It forms crystalline salts with acids.

Dimethylparamidobenzoic acid, $C_6H_4N(CH_3)_2CO_2H$, is obtained by heating the amido-acid with caustic potash, methyl iodide and wood spirit. It crystallizes in short, broad needles, melting at 235°, and combines with acids and bases, but is insoluble in acetic acid.[8]

Acetparamidobenzoic acid, $C_6H_4(NH.C_2H_3O)CO_2H$. Hofmann obtained this compound by the oxidation of acetparatoluide with potassium permanganate. It is slightly soluble in water, readily in alcohol, and crystallizes in needles, which melt with decomposition at 250°.[9] On boiling with hydrochloric acid it is converted into paramidobenzoic acid.[10]

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[1] Griess, *Ber. Deutsch. Chem. Ges.* xvi. 336.

[2] Fischer, *Ann. Chem. Pharm.* cxxvii. 142.

[3] Beilstein and Wilbrand, *ibid.* cxxviii. 264.

[4] Ladenburg, *Ber. Deutsch. Chem. Ges.* vi. 130.

[5] Beilstein and Reichenbach, *Ann. Chem. Pharm.* cxxxii. 144.

[6] Engler, *ibid.* cxlix. 302; Fricke, *Ber. Deutsch. Chem. Ges.* vii. 1322.

[7] Griess, *ibid.* viii. 861.

[8] Michler, *ibid.* ix. 401.

[9] *Ibid.* ix. 401.

[10] Kaiser, *ibid.* xviii. 2942.

Para-uramidobenzoic acid, $C_8H_8N_2O_3$, is formed at the same time as paracarbamidobenzoic acid by fusing paramidobenzoic acid with urea, or potassium cyanate with paramidobenzoic acid hydrochloride. It forms elongated plates, is scarcely soluble in cold, only very slightly in boiling water, more readily in hot alcohol. Concentrated nitric acid only forms one dinitro-compound.

Paracarbamidobenzoic acid, $C_{15}H_{12}N_2O_5$, is obtained by heating the preceding compound, and forms small needles which are insoluble in the ordinary solvents.

CHLORAMIDOBENZOIC ACIDS, $C_6H_3Cl(NH_2)CO_2H$.

	$Cl : NH_2$		Melting-point.
α)	2 : 5	small, readily soluble needles,[1] . .	212°
β)	3 : 6	long, almost insoluble needles,[2] . .	148°
δ)	3 : 5	needles,[3]	216°
ε)	4 : 3	small needles,[4]	212°

2145 The chloramidobenzoic acids corresponding to *γ*- and *ζ*-chloronitrobenzoic acids are unknown. Two others have, however, been prepared, one of which has been obtained from chlorisatin, and should be identical with the *β*-acid, but melts at 204°;[5] it will subsequently be mentioned. The second has been prepared by Griess together with the *ε*-acid by decomposing metadiazobenzoic acid imide, $C_6H_4N_3.CO_2H$, with hydrochloric acid; it crystallizes in small prisms and has the constitution $Cl : NH_2 = 2 : 3$.[6]

---

[1] Hübner and Biedermann, *Ann. Chem. Pharm.* cxlvii. 258; Rack and Wilken, *ibid.* ccxxii. 198.

[2] Cunze and Hübner, *ibid.* cxxxv. 111; Hübner and Weiss, *Ber. Deutsch. Chem. Ges.* vi. 175.

[3] Grube, *ibid.* x. 1703.

[4] Hübner and Biedermann; Raveill, *Ann. Chem. Pharm.* ccxxii. 177.

[5] Dorsch, *Journ. Prakt. Chem.* [2] xxxiii. 50.

[6] Griess, *Ber. Deutsch. Chem. Ges.* xix. 313.

BROMAMIDOBENZOIC ACIDS, $C_6H_3Br(NH_2)CO_2H$.

	Br : NH_2		Melting-point.
a)	2 : 5	broad needles [1]	180°
β)	3 : 6	long, slightly soluble needles [2] . .	208°
γ)	3 : 2	needles [3]	172°
δ)	4 : 3	light yellow needles [4]	225°
ε)	3 : 5	colourless, tough needles [5]	215°

IODAMIDOBENZOIC ACIDS, $C_6H_3I(NH_2)CO_2H$.

			Melting-point.
a)	3 : 2	brown needles	137°
β)	3 : 6	needles melting with decomposition	209°

These have been prepared from the iodonitrobenzoic acids and are converted by reduction into orthamidobenzoic acid.

NITRO-AMIDOBENZOIC ACIDS, $C_6H_3NO_2(NH_2)CO_2H$.

2146 Seven of the ten acids possessing this composition which are possible according to theory are known, and their constitution is shown on the next page. The first three have been obtained from meta-uramidobenzoic acid, which, as already mentioned, yields three dinitro-compounds. These cannot be directly separated, but on boiling with dilute ammonia are converted into the mononitro-uramidobenzoic acids, which can be separated by means of their barium salts:

$$C_8H_6(NO_2)_2N_2O_3 + H_2O = C_8H_7(NO_2)N_2O_3 + NO_2.OH.$$

They are re-converted by concentrated nitric acid into the

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[1] Burghard, *Ber. Deutsch. Chem. Ges.* viii. 560.

[2] Hübner and Mecker, *Zeitschr. Chem.* 1867, 564 ; Hübner, Ohly and Philipp, *Ann. Chem. Pharm.* cxliii. 241 ; Hübner and Petermann, *ibid.* cxlix. 133.

[3] *Ibid.*

[4] Burghard ; Raveill.

[5] Hesemann and Köhler, *Ann. Chem. Pharm.* ccxxii. 169.

[illegible]

$$[illegible] = [illegible] -NO-CO_2$$

$$[illegible] NH_2$$

$$[illegible] NH_2$$

[illegible] in water [illegible]

[illegible] 14 [illegible] scarcely [illegible] melt at [illegible]

[illegible]

284°. It is converted by the diazo-reaction into metanitrobenzoic acid, and by reduction into β-diamidobenzoic acid.

ε-Nitro-amidobenzoic acid was prepared by Griess from dinitro-ortho-uramidobenzoic acid, and by Hübner from the nitrosalicylic acid which melts at 228° by heating the ethyl ether with alcoholic ammonia; *ε-nitro-amidobenzamide*, $C_6H_3NO_2(NH_2)CO.NH_2$, is thus obtained, and crystallizes in small, yellow needles, melting at 140°; it is converted into the acid by boiling with baryta water.[1] Rhalis obtained it, together with paranitraniline, by heating the nitrobromobenzoic acid which melts at 179°—180° with ammonia.[2] It crystallizes from hot water in long, lustrous, yellow needles, melting at 270°. Ethyl nitrite converts it into metanitrobenzoic acid, and on reduction it yields *a*-diamidobenzoic acid.

ζ-Nitro-amidobenzoic acid. Hübner obtained the amide of this acid from the nitrosalicylic acid which melts at 144°; it crystallizes in yellow plates, melting at 109°, and on boiling with baryta water yields the acid, which is readily soluble in alcohol and crystallizes from hot water in long, yellow, silky needles, melting at 204°. Nitrous acid converts it into metanitrobenzoic acid.

η-Nitro-amidobenzoic acid is formed by the reduction of δ-dinitrobenzoic acid with ammonium sulphide,[3] and crystallizes from water in long, golden yellow needles, or small, compact prisms, melting at 208°. It is converted into metanitrobenzoic acid by ethyl nitrite, while metachlorobenzoic acid may be obtained from it by replacing the amido-group by chlorine and the nitroxyl by hydrogen; its constitution is thus established.

DINITRO-AMIDOBENZOIC ACIDS,

$C_6H_2(NO_2)_2(NH_2)CO_2H$.

2147 *Dinitro-orthamidobenzoic acid* or *Dinitro-anthranilic acid* ($NO_2 : NO_2 = 3 : 5$) is prepared by the action of ammonia on the ether of dinitrosalicylic acid. It is slightly soluble in alcohol, and crystallizes from it in lustrous, golden scales, melting at 256°.[4]

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[1] *Ann. Chem. Pharm.* xix. 21.

[2] *Ibid.* cxcviii. 112.

[3] Böcker, Grube and Rollwage, *Ber. Deutsch. Chem. Ges.* x. 1703; *Ann. Chem. Pharm.* ccxxii. 81.

[4] Salkowski, *Ann. Chem. Pharm.* clxxiii. 40.

Dinitroparamidobenzoic acid, ($NO_2 : NO_2 = 2 : 6$). Cahours, in 1849, found that an acid soluble in ammonia is formed by the action of fuming nitric acid on nitranisic acid, in addition to dinitro-anisol and trinitro-anisol (Part III., p. 125). This substance being of a splendid golden yellow colour, he named it chrysanisic acid, $C_7H_5N_3O_7$, looking upon it as a homologue of picric acid.[1] After trinitrocresol had been prepared, Kolbe suggested that it is identical with chrysanisic acid,[2] but Beilstein and Kellner showed that this is not the case, since the latter has the formula $C_7H_5N_3O_6$, and differs from the isomeric trinitro-toluene, which was prepared and described by Wilbrand.[3]

The actual constitution of chrysanisic acid was determined by Salkowski, who found that it is not contained in the product of the action of nitric acid on nitranisic acid, but is formed by the action of ammonia on dinitro-anisic acid:[4]

$$C_6H_2(OCH_3)(NO_2)_2CO_2H + NH_3 = C_6H_2(NH_2)(NO_2)_2CO_2H + HO.CH_3.$$

It may also be obtained by the oxidation of dinitropara-toluidine,[5] and crystallizes from hot water, in which it is only very slightly soluble, in fine needles, and from alcohol in lustrous golden, rhombic plates, melting at 259°. On heating to 200°—210° with fuming hydrochloric acid, β-trichlorobenzoic acid is formed, and with nitric acid it yields picric acid, while the dinitro-anisic acid from which it is prepared is converted into β-dinitrophenol when heated with water to 170°.[6]

DIAMIDOBENZOIC ACIDS, $C_6H_3(NH_2)_2CO_2H$.

2148 The formation of these has been already mentioned under the dinitro- and nitro-amido-benzoic acids. The numbers signify the position of the amido groups.

a-Diamidobenzoic acid (2 : 5) is slightly soluble in alcohol and hot water, and crystallizes in very small prisms, which decompose on heating with formation of paradiamidobenzene.

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[1] *Ann. Chim. Phys.* [3] xxvii. 454.
[2] *Lehrb. Org. Chem.* ii. 145.
[3] *Ann. Chem. Pharm.* cxxviii. 161.
[4] *Ibid.* clxiii. 1.
[5] Friederici, *Ber. Deutsch. Chem. Ges.* xi. 1975
[6] Salkowski and Rudolph, *ibid.* x. 1254.

β-Diamidobenzoic acid (3 : 4) crystallizes from hot water in small plates, which melt at 211°, and decompose at a higher temperature, more easily when mixed with powdered glass or lime, into carbon dioxide and orthodiamidobenzene.

γ-Diamidobenzoic acid (2 : 3) forms long, yellowish white needles, and also yields orthodiamidobenzene on heating.

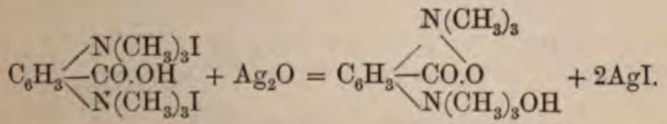
δ-Diamidobenzoic acid (3 : 5) is slightly soluble in water, more readily in alcohol, and crystallizes in long needles which melt at 228° when gradually heated, but at 236° when rapidly heated,[1] and are carbonized at a higher temperature with evolution of ammonia. On heating with caustic baryta, it decomposes into carbon dioxide and metadiamidobenzene. It decomposes carbonates and forms salts which crystallize well. Its dilute aqueous solution is coloured deep yellow by nitrous acid (p. 263).

Barium diamidobenzoate, $2(C_6H_3(NH_2)_2CO_2)_2Ba + 3H_2O$, crystallizes in yellowish prisms, which are readily soluble in water. Like its isomerides, it also combines with acids.

δ-Diamidobenzoic acid hydrochloride, $C_6H_3(CO_2H)(NH_2)_2(ClH)_2$, is readily soluble in water, but only slightly in hydrochloric acid, and crystallizes in needles.

δ-Diamidobenzoic acid sulphate, $(C_6H_3(CO_2H)(NH_2)_2)SO_4H_2$, forms white needles or prisms, which are slightly soluble in water and still less so in alcohol.[2]

Hexmethyl-δ-diamidobenzoic acid, or, as Griess called it, sixfold methylated diamidobenzoic acid, is not an acid in its properties but a strongly alkaline ammonium hydroxide and, at the same time, a salt. The iodide is formed by the action of methyl iodide and caustic potash on a solution of δ-diamidobenzoic acid in methyl alcohol. It crystallizes in six-sided tablets or plates, and when treated in concentrated aqueous solution with silver oxide yields the free base :



$$C_6H_3\begin{cases}N(CH_3)_3I\\CO.OH\\N(CH_3)_3I\end{cases} + Ag_2O = C_6H_3\begin{cases}N(CH_3)_3\diagdown\\CO.O\\N(CH_3)_3OH\end{cases} + 2AgI.$$

It is obtained on evaporation as a crystalline mass, which consists of small plates, is very hygroscopic and behaves like caustic potash. The carbonate crystallizes from alcohol in small plates, is readily soluble in water and has an alkaline reaction.[1]

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[1] Hübner, *Ann. Chem. Pharm.* ccxxii. 85.

[2] Griess, *ibid.* cliv. 328.

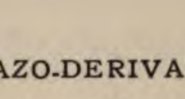
TRI-AMIDOBENZOIC ACID, $C_6H_2(NH_2)_3CO_2H$.

Salkowski obtained this compound by the reduction of chrysanisic acid with tin and hydrochloric acid. It crystallizes from boiling water in fine, lustrous needles, and decomposes on heating into carbon dioxide and triamidobenzene. Its solution has an acid reaction, and it is at once a monobasic acid and a diacid base.

DIAZO-DERIVATIVES OF BENZOIC ACID.

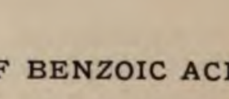
2149 The amidobenzoic acids behave in some respects like amido-acetic acid and its homologues, and in others like aniline, since they can be easily converted into diazobenzoic acids. For this purpose, a magma of amidobenzoic acid and nitric acid is well cooled by ice and saturated with nitrogen trioxide, the nitrate formed being then precipitated with alcohol and ether. Other salts are obtained in a similar manner. The sulphates are best prepared by dissolving the nitrate in a cold mixture of equal parts of water and sulphuric acid, and precipitating in crystals by the addition of strong alcohol and then ether.[2] The diazobenzoic acids, which, like the diazophenols, only exist as anhydrides, are obtained from these salts by the action of caustic potash. They also form double salts, which Griess looks upon as basic salts:

Diazobenzoic acid.



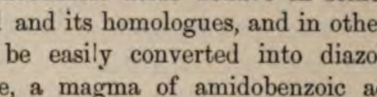
$$C_6H_4\left\langle\begin{array}{l} N=N \\ \quad\;\;\, | \\ CO-O \end{array}\right.$$

Diazobenzoic acid nitrate.



$$C_6H_4\left\langle\begin{array}{l} N{=}N.NO_3 \\ CO.OH. \end{array}\right.$$

Diazobenzoic acid seminitrate.



$$C_6H_4\left\langle\begin{array}{ll} N{=}N.O.CO.C_6H_4 & \\ & \;\;| \\ CO.OH & N{=}N.NO_3. \end{array}\right.$$

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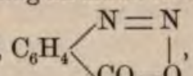
[1] Griess, *Ber. Deutsch. Chem. Ges.* vii. 39; Brühl, *ibid.* viii. 485.

[2] Griess, *ibid.* xviii. 960.

The substituted amidobenzoic acids, as well as their amides, nitrils, &c., also form diazo-compounds.

Orthodiazobenzoic acid nitrate, $NO_3.N_2.C_6H_4.CO_2H$, is readily soluble in water, and crystallizes in rhombic or six-sided tablets, or prisms, which explode violently on heating. When it is repeatedly dissolved in water and precipitated with alcohol and ether, or when an alcoholic solution of anthranilic acid is treated with nitrogen trioxide, *orthodiazobenzoic acid seminitrate*, $NO_3.N_2.C_6H_4.CO_2.N_2.C_6H_4.CO_2H$, is formed; it crystallizes in long, white needles, and detonates violently when heated.[1]

Metadiazobenzoic acid nitrate crystallizes in prisms, which are slightly soluble in cold water.[2] On adding an alkali to its solution, a precipitate of *metadiazobenzoic acid*,  $C_6H_4\left<\begin{matrix}N=N\\ \quad\ |\\ CO-O\end{matrix}\right.$, is thrown down.

This forms a yellow mass which is very unstable.

Metadiazobenzoic acid sulphate, $HSO_4.N_2.C_6H_4.CO_2H$, forms long, narrow plates, which are readily soluble in water. When it is repeatedly precipitated from aqueous solution by the addition of alcohol and ether, it becomes converted into the basic salt, to which Griess has given the formula $5C_7H_4N_2O_2, 2SO_4H_2$.[3] According to Beilstein it is probably $2(C_7H_5N_2O_2)_2SO_4+C_7H_5N_2O_2(OH)$.[4] It crystallizes in small needles.

When the normal sulphate is heated, it decomposes with a violent evolution of gas and formation of free sulphuric acid, sulphoxybenzoic acid, and a very stable compound, $C_{14}H_{10}SO_8$,[5] which probably has the following constitution: $SO_2(C_6H_3(OH)CO_2H)_2$.

Metadiazobenzoic acid platinichloride, $(C_7H_5N_2O_2)_2PtCl_6$, is obtained by the addition of platinum chloride to a solution of the nitrate; it crystallizes in yellow prisms.

Metadiazobenzoic acid perbromide, $Br_2N—BrN.C_6H_4.CO_2H$, is precipitated as an oil by the addition of a solution of bromine in hydrobromic acid to a solution of the nitrate; it soon solidifies to a mass of yellow prisms, and is converted by ammonia into diazobenzoic acid imide.

Metadiazobenzamide nitrate, $NO_3.N_2.C_6H_4.CO.NH_2$, crystallizes in white, explosive needles.

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[1] Griess, *Ann. Chem. Pharm.* cxvii. 39, cxxxv. 121; *Ber. Deutsch. Chem. Ges.* ix. 1653.

[2] Griess, *Ann. Chem. Pharm.* cxx. 126.

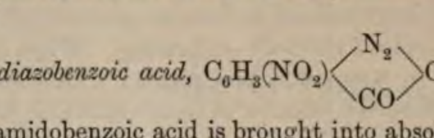
[3] *Ber. Deutsch. Chem. Ges.* ix. 1655.

[4] *Handb. Org. Chem.* 1139.

[5] *Jahresb. Chem.* 1864, 351.

Metadiazobenzonitril nitrate, $NO_3.N_2.C_6H_4.CN$, forms explosive needles or prisms which are only slightly soluble in cold water.[1]

Paradiazobenzoic acid nitrate also crystallizes in white, explosive prisms.[2]

Nitrodiazobenzoic acid,  $C_6H_3(NO_2)\left\langle\begin{matrix}N_2\\CO\end{matrix}\right\rangle O$, is formed when δ-nitro-amidobenzoic acid is brought into absolute alcohol nearly saturated with nitrogen trioxide; it forms light yellow, explosive plates.[3]

Diazobenzene-amidobenzoic acid, $C_6H_5.N{=}N.NH.C_6H_4.CO_2H$, is obtained by mixing aqueous solutions of diazobenzene nitrate and metamidobenzoic acid.[4] According to Griess, this compound is identical with that obtained by the action of aniline on metadiazobenzoic acid, and which was therefore considered to have the constitution $C_6H_5.NH.N{=}N.C_6H_4.CO_2H$. Griess, however, expresses the constitution of both compounds by the same formula, $C_6H_5.NH{=}NH{=}NH.C_6H_4.CO_2H$ (Part III., p. 269).[5]

By either process, a yellow, crystalline substance is obtained, which separates from ether in small plates, and is decomposed by hydrochloric acid with formation of metamidobenzoic acid, metachlorobenzoic acid, metahydroxybenzoic acid, aniline, phenol and nitrogen. The acid forms a yellow solution in alkalis; on the addition of barium chloride to its ammoniacal solution, which must not be too dilute, the barium salt separates out in small, light yellow crystals.

Metadiazo-amidobenzoic acid, $CO_2H.C_6H_4.NH.N{=}N.C_6H_4.CO_2H$, is formed by the action of metamidobenzoic acid on metadiazobenzoic acid,[6] and therefore as an intermediate product when nitrogen trioxide is passed into an alcoholic solution of metamidobenzoic acid.[7] It forms orange-yellow, crystalline granules, which are almost insoluble in water, alcohol, ether, &c., and detonate at 180°. It is soluble in alkalis, and is reprecipitated by acids, even acetic acid. On boiling with hydrochloric acid, it decomposes with evolution of nitrogen into metamidobenzoic acid and metachlorobenzoic acid. It is a tolerably strong dibasic acid and decomposes carbonates.

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[1] Griess, *Ber. Deutsch. Chem. Ges.* ii. 370.

[2] *Jahresb. Chem.* 1864, 353.

[3] Salkowski, *Ann. Chem. Pharm.* clxxiii. 63.

[4] Griess, *ibid.* cxxxvii. 63.

[5] *Ber. Deutsch. Chem. Ges.* vii. 1619.

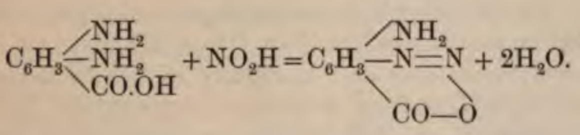
[6] *Jahresb. Chem.* 1864, 353.

[7] *Ann. Chem. Pharm.* cxvii. 1.

Paradiazo-amidobenzoic acid was obtained by Beilstein and Wilbrand by treating a saturated alcoholic solution of paramidobenzoic acid with a solution of nitrogen trioxide in alcohol. It is an orange-yellow, crystalline powder, which is only slightly soluble in boiling alcohol.[1]

Isomeric compounds are formed from metadiazobenzoic acid and paramidobenzoic acid, and from paradiazobenzoic acid and metamidobenzoic acid (Griess).

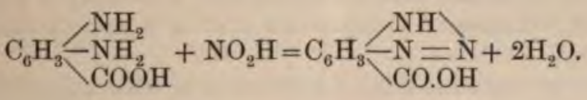
2150 *The Action of Nitrous Acid on the Diamidobenzoic Acids.* When sodium nitrite is added to a neutral solution of α-diamidobenzoic acid, which contains the amido-group in the para-position, *paramidodiazobenzoic acid* is formed:



$$C_6H_3\begin{cases}NH_2\\NH_2\\CO.OH\end{cases} + NO_2H = C_6H_3\begin{cases}NH_2\\N{=}N\\CO{-}O\end{cases} + 2H_2O.$$

It is insoluble in ether, slightly soluble in hot alcohol, readily in hot water, and crystallizes in fine needles or four-sided plates, which are brass coloured, have a very bitter taste, and detonate on heating. It does not combine with bases, but forms crystalline salts with acids; it also combines with amido-bases and phenols to form azo-compounds.[2]

Nitrous acid acts upon the two orthodiamidobenzoic acids (β and γ) in the following manner:



$$C_6H_3\begin{cases}NH_2\\NH_2\\COOH\end{cases} + NO_2H = C_6H_3\begin{cases}NH\\N{=}N\\CO.OH\end{cases} + 2H_2O.$$

The *diazo-imidobenzoic acids* obtained in this manner crystallize in needles and are powerful acids, the barium salts of which are only slightly soluble in cold water.[3]

Metadiamidobenzoic acid corresponds exactly with metadiamidobenzene in its behaviour towards nitrous acid. In a very dilute solution a yellow colouration is produced, and this reaction is so delicate that one part of nitrous acid can be detected in five million parts of water. In concentrated solutions a reddish-brown precipitate of *triamido-azobenzoic acid* is formed:

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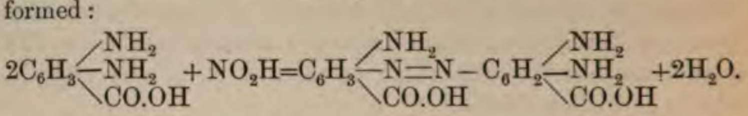
[1] *Ann. Chem. Pharm.* cxxviii. 269.

[2] Griess, *Ber. Deutsch. Chem. Ges.* v. 200, xvii. 603.

[3] Griess, *ibid.* ii. 436.



$$2C_6H_3\begin{cases}NH_2\\NH_2\\CO.OH\end{cases} + NO_2H = C_6H_3\begin{cases}NH_2\\N{=}N-C_6H_2\begin{cases}NH_2\\NH_2\\CO.OH\end{cases}\\CO.OH\end{cases} + 2H_2O.$$

This substance is soluble in alkalis, and is reprecipitated by acids.[1]

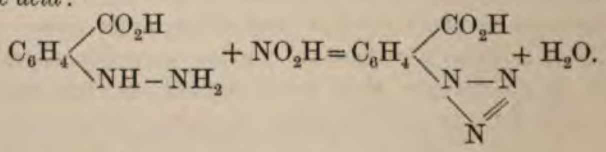
HYDRAZINEBENZOIC ACIDS, $C_6H_4\begin{cases}NH.NH_2\\CO.OH.\end{cases}$

2151 These compounds are obtained from the amidobenzoic acids by the methods which are employed in the preparation of phenylhydrazine from aniline (Part III., p. 275).

Orthohydrazinebenzoic acid is slightly soluble in alcohol and ether, and crystallizes from hot water in fine needles. It reduces Fehling's solution and salts of silver and mercury in the cold, and combines with bases and acids. When it is gently heated with concentrated hydrochloric acid or heated rapidly to 220°—230° in a stream of carbon dioxide, the anhydride is formed.

Orthobenzoylhydrazide, $C_6H_4\begin{cases}NH\\CO\end{cases}\!NH$, forms crystals which are slightly soluble in alcohol, ether, and hot water, have an acid reaction, and are readily dissolved by alkalis. It does not combine with acids, and does not reduce salts of mercury or Fehling's solution, but causes a precipitation of silver from an ammoniacal solution.[2]

Metahydrazinebenzoic acid is insoluble in ether, slightly soluble in alcohol and hot water, and crystallizes in small, yellowish plates, which melt with decomposition at 186°. It has an acid reaction, combines with acids and bases, and reduces Fehling's solution. Nitrous acid converts it into the *imide of metadiazobenzoic acid*:



$$C_6H_4\begin{cases}CO_2H\\NH-NH_2\end{cases} + NO_2H = C_6H_4\begin{cases}CO_2H\\N-N\\ \;\;\diagdown\!\!\diagup\\ \;\;\;N\end{cases} + H_2O.$$

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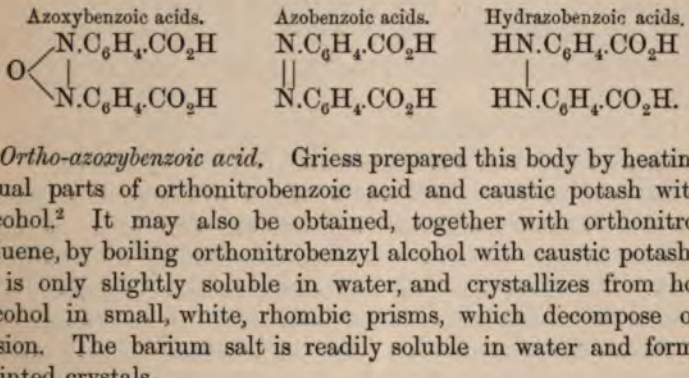
[1] Voit, *Ann. Chem. Pharm.* xcix. 100; Griess, *ibid.* cliv. 334; *Ber. Deutsch. Chem. Ges.* xvii. 606.

[2] Fischer, *Ber. Deutsch. Chem. Ges.* xiii. 679.

This is a monobasic acid, which is scarcely soluble in cold, slightly in hot water, and readily in alcohol; it crystallizes in thin plates, melting at 160°. Metahydrazinebenzoic acid is decomposed in presence of diazobenzene nitrate with formation of diazobenzoic acid imide, metamidobenzoic acid, diazobenzeneimide and aniline.[1]

AZO-DERIVATIVES OF BENZOIC ACID.

2152 These are formed, like other azo-compounds, by the reduction of the corresponding nitro-derivatives, the following substances being obtained:



$$O\begin{cases} N.C_6H_4.CO_2H \\ N.C_6H_4.CO_2H \end{cases} \qquad \begin{array}{l} N.C_6H_4.CO_2H \\ \| \\ N.C_6H_4.CO_2H \end{array} \qquad \begin{array}{l} HN.C_6H_4.CO_2H \\ | \\ HN.C_6H_4.CO_2H. \end{array}$$

Ortho-azoxybenzoic acid. Griess prepared this body by heating equal parts of orthonitrobenzoic acid and caustic potash with alcohol.[2] It may also be obtained, together with orthonitrotoluene, by boiling orthonitrobenzyl alcohol with caustic potash.[3] It is only slightly soluble in water, and crystallizes from hot alcohol in small, white, rhombic prisms, which decompose on fusion. The barium salt is readily soluble in water and forms pointed crystals.

Ortho-azobenzoic acid is formed by the action of sodium amalgam on a solution of sodium orthonitrobenzoate. It is almost insoluble in water and crystallizes from hot alcohol in fine, dark-yellow needles, which melt at 237° with partial decomposition. Its yellow barium salt crystallizes with seven molecules of water in prisms, or with nine molecules in needles.[4]

Orthohydrazobenzoic acid is obtained by treating a concentrated alkaline solution of azoxybenzoic acid with sodium amalgam.[5] It crystallizes from alcohol in colourless, elliptical plates or microscopic prisms, and is readily oxidized to the preceding compound.

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[1] Griess, *Ann. Chem. Pharm.* ix. 1657; Fischer, *ibid.* xvi. 1335.
[2] *Ibid.* vii. 1611.
[3] Jaffé, *Hoppe-Seyler's Zeitschr.* ii. 57.
[4] Griess, *Ber. Deutsch. Chem. Ges.* x. 1869.
[5] Griess, *ibid.* vii. 1612.

Metazoxybenzoic acid is insoluble in water, slightly soluble in alcohol and ether, and forms microscopic needles or plates. Its barium salt is an almost insoluble precipitate.[1]

Metazobenzoic acid was first prepared by Neubauer by the oxidation of metamidobenzoic acid with potassium permanganate, but was not further investigated.[2] Beilstein and Wilbrand then found that an acid is formed by the action of zinc on an alkaline solution of metanitrobenzoic acid, which, according to its composition, lies between nitro- and amido-benzoic acids.[3] Strecker, who prepared it by means of sodium amalgam, named it azobenzoic acid.[4] It is also formed by the action of zinc on ammonium metanitrobenzoate.[5] Acids separate it from its salts as a light-yellow, viscid precipitate, which becomes granular when heated with alcohol, and is only slightly soluble in water, alcohol, and ether. Its almost insoluble barium salt crystallizes in microscopic, rhombic plates containing five molecules of water.

On distillation with lime, azophenylene, $C_{12}H_8N_2$, is formed, while its copper salt yields azobenzene on dry distillation.[6]

Metahydrazobenzoic acid was obtained by Strecker by adding ferrous sulphate and then hydrochloric acid to an alkaline solution of the azo-acid. It is also formed by the continued action of sodium amalgam and other reducing agents. It is amorphous, insoluble in water, and only slightly soluble in alcohol. It is readily oxidized in alkaline solution to the preceding compound and, like hydrazobenzene, undergoes an intermolecular change (Part III., p. 295), when it is boiled with concentrated hydrochloric acid, diamidodiphenic acid, $C_{12}H_6(NH_2)_2(CO_2H)_2$, being formed.[7]

Parazobenzoic acid is almost insoluble in alcohol, water and ether, and forms a yellow or reddish precipitate, which becomes granular on boiling and melts at about 240°.[8] The barium salt is a flesh-coloured precipitate; azophenylene is formed when the calcium salt is distilled (Claus).

Parahydrazobenzoic acid is insoluble in water and crystallizes from alcohol in needles; its alkaline solution absorbs oxygen with formation of the azo-acid.

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[1] Griess, *Jahresber.* 1864, 352.

[2] *Ann. Chem. Pharm.* cvi. 70.

[3] *Ibid.* cxxviii. 267.

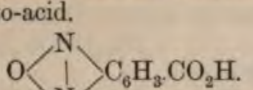
[4] *Ibid.* cxxix. 129.

[5] Sokolow, *Journ. Prakt. Chem.* xciii. 425; Liebert, *ibid.* xciii. 429.

[6] Claus, *Ber. Deutsch. Chem. Ges.* viii. 41.

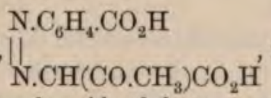
[7] Griess, *ibid.* vii. 1609; Schultz, *Ann Chem. Pharm.* cxcvi. 18.

[8] Reichenbach and Beilstein, *Ann. Chem. Pharm.* cxxix. 144; Bilfinger, *ibid.* cxxxv. 164.

Diazoxybenzoic acid,  $O\left<\begin{matrix}N\\ |\\ N\end{matrix}\right>C_6H_3.CO_2H$. When δ-dinitrobenzoic acid is dissolved in caustic soda and treated with sodium amalgam, the liquid becomes coloured black but remains perfectly clear, appearing brown when diluted. Acids added to this solution precipitate diazoxybenzoic acid as an amorphous, black powder, which is insoluble in water, alcohol, ether, &c., and detonates feebly on heating. The alkali salts form black solutions in water; the salts of other metals are black precipitates. The barium salt, when dried at 70°, becomes so strongly electrified that the particles continue in motion for hours; it loses this property at a higher temperature. Tin and hydrochloric acid reduce the acid to δ-diamidobenzoic acid.

Isodiazoxybenzoic acid is obtained from β-dinitrobenzoic acid and resembles the preceding compound, but is not attacked by tin and hydrochloric acid.[1]

Azonitromethanebenzoic acid, $NO_2.CH_2N{=}NC_6H_4.CO_2H$, is formed when an aqueous solution of pure metadiazobenzoic acid nitrate is mixed with a dilute solution of nitromethane in caustic potash, and the whole treated with an excess of hydrochloric acid after standing for some time. It is readily soluble in hot alcohol and ether, slightly in boiling water, and crystallizes in stellate groups of yellowish-red plates, which are almost tasteless and detonate on heating. Silver nitrate added to its ammoniacal solution produces a deep red precipitate.[2]

Azo-aceto-acetic benzoic acid,  $\begin{matrix}N.C_6H_4.CO_2H\\ \|\\ N.CH(CO.CH_3)CO_2H\end{matrix}$, is obtained by the action of metadiazobenzoic acid sulphate on aceto-acetic ether, the method described for the preparation of the preceding compound being followed. It is thrown down by hydrochloric acid as a light yellow precipitate consisting of microscopic spheres, and is insoluble in boiling water, crystallizing from hot alcohol in narrow plates or small needles, which have a bitter taste. On careful heating it fuses to an oil, which solidifies on cooling to a waxy mass, but at a higher temperature it detonates feebly, a large quantity of carbon separating out. Its silver salt is a light yellow, amorphous precipitate.

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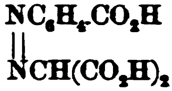
[1] Meyer and Michler, *Ann. Chem. Pharm.* clxxv. 152; *Ber. Deutsch. Chem. Ges.* vi. 746, vii. 422.

[2] Griess, *ibid.* xviii. 961.

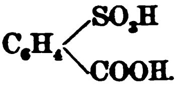
Azomalonic-benzoic acid,



$$\begin{array}{l} NC_6H_4.CO_2H \\ \| \\ NCH(CO_2H)_2 \end{array}$$

. Griess obtained this compound in a similar manner from malonic ether. Hydrochloric acid separates it from the product as an amorphous, fiery yellowish red precipitate, which crystallizes from hot alcohol in microscopic plates. On heating it froths up and chars.

MONOSULPHOBENZOIC ACIDS,



$$C_6H_4\begin{cases} SO_3H \\ COOH. \end{cases}$$

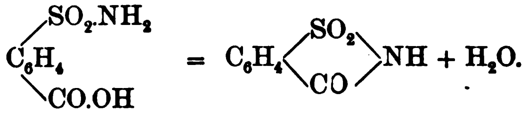
2153 *Orthosulphobenzoic acid* is formed, together with orthosulphamidobenzoic acid, when orthotoluenesulphamide is oxidized with potassium permanganate. On the addition of hydrochloric acid to the filtrate, the anhydride of the sulphamide separates out, while acid potassium orthosulphobenzoate remains in solution and is deposited in large monoclinic tablets.[1]

It may also be obtained by heating the diazo-compound of anthranilic acid with an alcoholic solution of sulphur dioxide.[2]

It crystallizes from water in large, monoclinic tablets, which do not deliquesce in the air and melt at 240° with decomposition. On fusion with caustic potash salicylic acid is formed.[3]

Acid barium orthosulphobenzoate, $(C_7H_5SO_3)_2Ba + 2H_2O$, crystallizes in needles, and is less soluble in water than the normal salt.

Orthosulphamidobenzoic acid is not known in the free state, as when it is liberated from its salts by the addition of an acid it is immediately converted into the anhydride:



$$C_6H_4\begin{cases} SO_2.NH_2 \\ CO.OH \end{cases} = C_6H_4\begin{cases} SO_2 \\ CO \end{cases}NH + H_2O.$$

This body is slightly soluble in cold, more readily in hot water and alcohol, and forms crystals which melt at 220° and are sweeter than sugar. The salts, which are readily soluble in water, have also a sweet taste. When the anhydride, which is called *benzoylsulphimide*, is heated to 150° with hydrochloric acid, it is converted into orthosulphobenzoic acid. It is not attacked by phosphorus pentachloride.

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[1] Remsen, *Ann. Chem. Pharm.* clxxviii. 293; Fahlberg and Remsen, *Ber. Deutsch. Chem. Ges.* xii. 471.

[2] Wiesinger, *ibid.* xii. 1349.

[3] Böttinger, *ibid.* viii. 374.

According to Fahlberg and List[1] it is a powerful antiseptic, and, since a very dilute solution of it is as sweet as a concentrated solution of cane sugar, they believe that it may find an extended application. It could thus be used as a sweetening agent in the diet of patients suffering from diabetes and in many other cases as a cheap substitute for sugar. They propose for it the unsuitable name of *saccharin*, which has also been given (Part II., p. 547) to the lactone of saccharic acid.

2154 *Metasulphobenzoic acid.* In 1834 Mitscherlich found that benzoic acid combines with anhydrous sulphuric acid, SO_3, to form an acid which can be heated to above 150°, and boiled with water without decomposition. Its barium salt can also be boiled with caustic potash without losing sulphuric acid. He says, "I propose to name it provisionally benzoylsulphuric acid, since the complexity of its composition necessitates a name which gives a clue to its constitution without indicating it fully."[2]

Fehling, who investigated its salts more closely, observed that when heated with an excess of caustic potash until complete decomposition has taken place, it yields a residue containing both sulphite and sulphate of potassium, a behaviour which is characteristic of the salts of hyposulphuric acid. "This acid, therefore, contains hyposulphuric and not sulphuric acid," and he therefore called it benzoylhyposulphuric acid.[3]

It was then investigated with great care by Limpricht and v. Uslar, who recognised it as a sulphonic acid.[4]

It is also formed by the action of sulphuric acid on benzonitril[5] and benzoyl chloride,[6] as well as by heating the latter with silver sulphate;[7] and by treating metadiazo-amidobenzoic acid with an alcoholic solution of sulphur dioxide.[8]

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[1] *Journ. Soc. Chem. Ind.* iv. 608; *Ber. Deutsch. Chem. Ges.* xix. Ref. 374.
[2] *Ann. Chem. Pharm.* xii. 314.
[3] *Ibid.* xxvii. 322.
[4] *Ibid.* cii. 239; cvi. 27.
[5] Buckton and Hofmann, *ibid.* c. 155.
[6] Oppenheim, *Ber. Deutsch. Chem. Ges.* iii. 735.
[7] Carius and Kämmerer, *Ann. Chem. Pharm.* cxxxi. 155; Ador and Oppenheim, *Ber. Deutsch. Chem. Ges.* iii. 738; Kämmerer, *ibid.* iv. 219.
[8] Vollbrecht and Wiesinger, *ibid.* x. 715.

In order to prepare metasulphobenzoic acid, the vapour of sulphur trioxide is passed over benzoic acid, which has been previously fused and powdered, until a transparent mass is formed; or two parts of benzoic acid are heated with one part of fuming sulphuric acid for some time. The product then contains some parasulphobenzoic acid in addition to metasulphobenzoic acid and free sulphuric acid.[1] It is diluted with water, neutralized with barium carbonate and filtered, the filtrate being then heated and treated with hydrochloric acid. The acid salt of the para-acid crystallizes out first on cooling, and then that of the meta-acid, which is purified by recrystallization. The product of the reaction may also be saturated with milk of lime, the filtrate treated with potassium carbonate, and the potassium salt which is thus obtained, recrystallized.[2] Metasulphobenzoic acid is a colourless, crystalline mass, which deliquesces in moist air, but solidifies again in dry air. It is not altered by boiling nitric acid. On fusion with potash, metahydroxybenzoic acid is formed (Barth), while with sodium formate it yields isophthalic acid (v. Meyer).

The Metasulphobenzoates. Metasulphobenzoic acid is a powerful dibasic acid, which decomposes even barium chloride and barium nitrate. Its normal salts are usually readily soluble, while the acid salts dissolve much less easily.

Normal potassium metasulphobenzoate, $C_7H_4SO_5K_2$, forms deliquescent crystals; the acid salt, $C_7H_5SO_5K$, crystallizes in long needles, which contain two and half or five molecules of water and are readily soluble in water and alcohol.[3]

Normal barium metasulphobenzoate, $C_7H_4SO_5Ba + 3H_2O$, is very soluble, and can with difficulty be obtained in well-developed crystals; it is usually deposited in crusts. The acid salt, $(C_7H_5SO_5)_2Ba + 3H_2O$, dissolves in 20 parts of cold water, readily in hot water and alcohol, and crystallizes in monoclinic prisms.

Normal lead metasulphobenzoate, $C_7H_4SO_5Pb + 2H_2O$, is much more readily soluble in hot water than in cold, and forms fine, radiating crystals, resembling those of wavellite.

Silver metasulphobenzoate, $C_7H_4SO_5Ag_2 + H_2O$, crystallizes in yellow prisms which readily dissolve.

Normal ethyl metasulphobenzoate, $C_7H_4SO_5(C_2H_5)_2$, is prepared from the chloride of the acid and absolute alcohol, and forms a thick liquid which has a faint ethereal odour, and decomposes on heating. It is soluble in water, and its solution decomposes when heated into alcohol and the acid.

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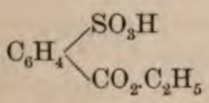
[1] *Ann. Chem. Pharm.* clxxviii. 275.

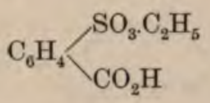
[2] Barth, *ibid.* cxlviii. 33.

[3] Otto, *ibid.* cxxii. 155.

Acid ethyl metasulphobenzoate or *Ethyl metasulphobenzoic acid*, $C_7H_5SO_5.C_2H_5$. The ammonium salt of this acid, $C_7H_4SO_5(NH_4).C_2H_5$, is obtained by passing ammonia into an alcoholic solution of the normal ether or by the action of alcoholic ammonia on the chloride. It crystallizes in large, four-sided, transparent tablets. If the ammonia be precipitated with platinum chloride, and the excess of platinum removed by sulphuretted hydrogen, a solution of the free acid is obtained; its salts crystallize well and are readily soluble. Its constitution is probably represented by the former of the two following formulæ:

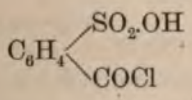


$$C_6H_4\left\langle\begin{array}{l}SO_3H\\CO_2.C_2H_5\end{array}\right.$$



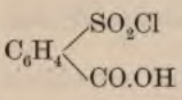
$$C_6H_4\left\langle\begin{array}{l}SO_3.C_2H_5\\CO_2H\end{array}\right.$$

Metasulphobenzoyl chloride, $C_7H_4SO_3Cl_2$, is obtained by heating the dry acid with phosphorus pentachloride; the phosphorus oxychloride is then distilled off and the residue washed with water. It is a thick, oily liquid, which has a faint but unpleasant odour, and decomposes on distillation into sulphur dioxide and metachlorobenzoyl chloride. The latter is also formed when the compound is heated to 140°—150° with phosphorus pentachloride. When it is allowed to stand for some time in contact with water or when the acid is acted upon by one molecule of phosphorus pentachloride, the monochloride is formed:



$$C_6H_4\left\langle\begin{array}{l}SO_2.OH\\COCl\end{array}\right.$$

or

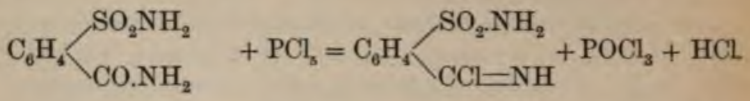


$$C_6H_4\left\langle\begin{array}{l}SO_2Cl\\CO.OH\end{array}\right.$$

This separates from ether in warty masses, and is decomposed by boiling water, &c., with formation of metasulphobenzoic acid.

Metasulphobenzamide, $C_7H_4SO_3(NH_2)_2$, is formed by the action of concentrated aqueous ammonia on the chloride. It is almost insoluble in cold water and crystallizes from hot water or ordinary alcohol in needles containing a molecule of water, while it separates from absolute alcohol in small, vitreous, anhydrous crystals.

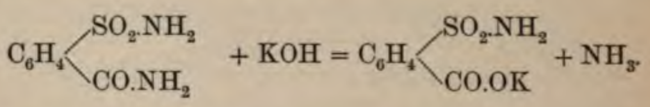
When it is heated with phosphorus pentachloride the following reaction takes place:



$$C_6H_4\begin{cases}SO_2NH_2\\CO.NH_2\end{cases} + PCl_5 = C_6H_4\begin{cases}SO_2.NH_2\\CCl{=}NH\end{cases} + POCl_3 + HCl.$$

The imido-chloride which is thus formed has not been obtained pure;[1] it decomposes on distillation with formation of metachlorobenzonitril, while ammonia or water converts it into *sulphamidobenzonitril*, $CN.C_6H_4.SO_2.NH_2$, which separates from alcohol in crystals, melting at 152°—153°.

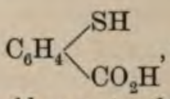
Metasulphamidobenzoic acid, $C_7H_7NSO_4$, is formed when the nitril or amide is heated with caustic potash solution:



$$C_6H_4\begin{cases}SO_2.NH_2\\CO.NH_2\end{cases} + KOH = C_6H_4\begin{cases}SO_2.NH_2\\CO.OK\end{cases} + NH_3.$$

It is slightly soluble in cold water, and crystallizes from a hot solution in scales resembling those of potassium chlorate and melting above 200°. It is a monobasic acid, and forms crystallizable salts.

Ethyl metasulphamidobenzoate, $C_7H_6(C_2H_5)NSO_4$, is obtained by heating the silver salt with ethyl iodide, or by passing hydrochloric acid into an alcoholic solution of the acid. It is also formed when ammonia is passed into a solution of sulphobenzoyl chloride in a mixture of alcohol and ether. It crystallizes from alcohol in monoclinic prisms.[2]



Metathiohydrobenzoic acid, $C_6H_4\begin{cases}SH\\CO_2H\end{cases}$, is prepared by the action of tin and hydrochloric acid on metasulphobenzoyl chloride. It is tolerably soluble in water, more readily in alcohol, and sublimes, when heated in a current of carbon dioxide, in flat needles, melting at 146°—147°. It oxidizes when exposed to the air in a moist state, or more rapidly when acted upon by bromine water, to *metadithiobenzoic acid*, $S_2(C_6H_4.CO_2H)_2$, which is scarcely soluble in water, and only slightly in alcohol, crystallizing from the latter in short needles which melt at 246°—247°.[3]

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[1] Huth and Wallach, *Ber. Deutsch. Chem. Ges.* ix. 427.
[2] Hart, *Amer. Chem. Journ.* i. 342.
[3] Frehrichs, *Ber. Deutsch. Chem. Ges.* vii. 792.

2155 *Parasulphobenzoic acid* is obtained by the oxidation of paratoluenesulphonic acid; it is not necessary to employ pure material for its preparation, and the mixture of the three isomeric acids which is obtained by dissolving toluene in sulphuric acid may be conveniently made use of. The para-compound is the chief constituent of the mixture, and, together with the meta-acid, is readily oxidized, while the ortho-acid remains unaltered (Remsen).

One hundred grammes of toluene are dissolved in the smallest possible quantity of fuming sulphuric acid, the solution made up to five litres with water, and heated until it becomes colourless. Hydrochloric acid and barium chloride are then added to the filtrate and the precipitated acid barium salt purified by re-crystallization; 200 grammes of it are obtained in this way.[1]

It is also formed by the action of alcoholic sulphurous acid on paradiazobenzoic acid (Vollbrecht and Wiesinger).

Parasulphobenzoic acid is readily soluble in water, and crystallizes in needles, which are not deliquescent and melt with decomposition at about 200°. On fusion with caustic potash, parahydroxybenzoic acid is formed, while with potassium formate it yields terephthalic acid.

The potassium salt forms transparent needles which easily dissolve.

Normal barium parasulphobenzoate, $C_7H_4SO_5Ba+2H_2O$, crystallizes in small, tolerably soluble needles. The acid salt, $(C_7H_5SO_5)_2Ba+3H_2O$, is slightly soluble in hot water, and forms long, flat, lustrous needles.

Parasulphamidobenzoic acid, $C_6H_5\begin{cases}SO_2.NH_2\\CO.OH\end{cases}$, is formed by the oxidation of paratoluenesulphamide with chromic acid solution. It is almost insoluble in cold, slightly soluble in hot water, and readily in alcohol, crystallizing in long, flat, lustrous prisms.

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[1] Hart, *loc. cit.*

[illegible] in transparent crystals, [illegible] in water and crystal- [illegible]

[illegible] slowly [illegible] the remaining [illegible] ordinary temperature and [illegible]

$$[illegible] - H_2O.$$

[illegible] in water. [illegible]

$$[illegible] - [illegible]\,CO_2H$$

[illegible] in small prisms. It [illegible] resembling cream of tartar. [illegible]

[illegible] is obtained as [illegible] On heating [illegible] as a thick liquid [illegible]

[illegible] is formed by the [illegible] a crystalline [illegible] water [illegible]

$$[illegible] - 3H_2O.$$

[illegible] the oxidation of [illegible] potassium per- [illegible]

$$[illegible] = [illegible] - H_2O.$$

[illegible] which are readily [illegible] base, which is liberated by [illegible] which [illegible] When [illegible] is heated with an excess of [illegible] it decomposes with formation of benzoic acid and trimethylphosphine oxide.

---

[1] M. [illegible] and Patek, *Ber. Deutsch. Chem. Ges.* xiv. 405.

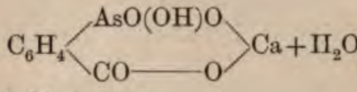
Dimethylphosphine-oxide benzoic acid, $C_6H_4.PO(CH_3)_2.CO_2H$, is formed by the oxidation of dimethyltolylphosphine oxide, and crystallizes in prisms which have a feebly acid taste, melt at 243°, sublime almost without decomposition, and are not easily attacked by caustic potash solution.[1]

BENZARSENIC ACIDS.

2160 *Benzarsenic acid*, $C_6H_4(AsO_3H_2)CO_2H$, is obtained by oxidizing paratolylarsenic acid in alkaline solution. It is only slightly soluble in water, and crystallizes in large, transparent tablets or nacreous plates. On heating the anhydride, *arsenobenzoic acid*, $C_6H_4(AsO_2)CO_2H$, is formed; this compound, which corresponds to paranitrobenzoic acid, is a yellowish powder, soluble in hot alcohol.

Acid potassium benzarsenate, $C_6H_4(AsO_3H_2)CO_2K + C_6H_4(AsO_3H_2)CO_2H$, crystallizes from hot water in transparent, triclinic tablets.

Acid calcium benzarsenate,



$$C_6H_4 \begin{array}{l} \diagup AsO(OH)O \diagdown \\ \diagdown CO\text{——}O \diagup \end{array} Ca + H_2O,$$

forms nacreous plates, slightly soluble in water.

Silver benzarsenate, $C_6H_4(AsO_3Ag_2)CO_2Ag$, is an amorphous precipitate, which yields the crystalline methyl ether on heating with methyl iodide.

Benzarsene chloride, $C_6H_4(AsCl_2)CO_2H$, is obtained by the action of phosphorus trichloride on the acid:

$$C_6H_4(AsO_3H_2)CO_2H + 2PCl_3 =$$
$$C_6H_4(AsCl_2)COCl + POCl_3 + P(OH)_3.$$

The product of the reaction is carefully treated with water, and yields the chloride, crystallizing in needles, which melt at 157°—158°, and are decomposed by boiling water.

Benzarsene iodide, $C_6H_4(AsI_2)CO_2H$, is formed by the action of hydriodic acid and phosphorus on the acid, and crystallizes from chloroform in yellow needles, melting at 153°.

Benzarsenious acid, $C_6H_4As(OH)_2CO_2H$, is prepared by dissolving the iodide in carbonate of soda and precipitating with hydrochloric acid; it is thrown down in crystals, and crystallizes

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[1] Michaelis and Czimatis, *Ber. Deutsch. Chem. Ges.* xv. 2018.

[illegible] in the [illegible] which are converted into the [illegible]

[illegible] crystallizes in [illegible] which [illegible] of water on heating [illegible] solution produces a white precipitate [illegible]

[illegible] is formed by the [illegible] with potassium permanganate [illegible] which are scarcely soluble in water, and [illegible] in alcohol and [illegible] acid. [illegible]

[illegible] [illegible] is obtained by heating the acid with [illegible] and amorphous phosphorus. It is a crystalline mass which dissolves in alcohol and ether, and [illegible]

[illegible] acid, $(C_6H_4.CO_2H)_2As.OH$, is prepared by decomposing the [illegible] with sodium [illegible] in the solution of [illegible] acid. It is obtained as a crystalline precipitate, which is slightly soluble in water, more readily in alcohol.

Calcium [illegible], [illegible]$As(C_6H_4.CO_2)_2Ca + 2H_2O$, is precipitated by alcohol from its aqueous solution as a white powder.

Tribenzarsenic acid, $(HO)_2As(C_6H_4.CO_2H)_3$, is formed when [illegible] is oxidized; it is [illegible] soluble in water and separates from alcohol in crusts, from ether in granular crystals.

Potassium tribenzarsenate, $AsO(C_6H_4.CO_2K)_3$, separates from alcohol in crystalline crusts, which are readily soluble in water.

Tribenzarsenious acid, or *Arsenotribenzoic acid*, $As(C_6H_4.CO_2H)_3$, is obtained by the reduction of tribenzarsenic acid with hydriodic acid and phosphorus; it crystallizes from ether in small colourless needles.

Sodium arsenotribenzoate, $As(C_6H_4.CO_2Na)_3 + 2H_2O$, crystallizes from hot water in short, fine needles. The silver salt is a yellowish precipitate.[1]

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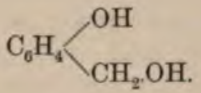
[1] La Coste, *Ann. Chem. Pharm.* ccviii. 1.

HYDROXYBENZYL GROUP.

HYDROXYBENZYL ALCOHOLS,

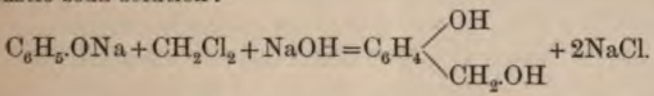


$C_6H_4\left\langle\begin{matrix}OH\\CH_2.OH.\end{matrix}\right.$

2161 *Orthohydroxybenzyl alcohol.* Piria, in 1845, found that salicin, which is contained in willow bark, is split up by the action of dilute acids or of emulsin (p. 130) into grape sugar and a new compound which he therefore named *saligenin:*[1]

$$C_{13}H_{18}O_7 + H_2O = C_6H_{12}O_6 + C_7H_8O_2.$$

This substance, which was subsequently also called *salicyl alcohol*, because it was found to stand to salicylic acid in the same relation as benzyl alcohol to benzoic acid, was obtained by Beilstein and Reineke by the action of sodium amalgam and water on salicyl aldehyde,[2] and Greene found that it is also formed when phenol is heated with methylene chloride and caustic soda solution:[3]



$$C_6H_5.ONa + CH_2Cl_2 + NaOH = C_6H_4\left\langle\begin{matrix}OH\\CH_2.OH\end{matrix}\right. + 2NaCl.$$

The decomposition of salicin by dilute acids cannot be employed for its preparation, since a portion of the alcohol is converted into saliretin (p. 280), and the following method, devised by Piria, is therefore made use of. Fifty parts of salicin are brought into 200 parts of water, and 3 parts of emulsin added, this substance being obtained by macerating pressed almonds with 3 parts of water for two hours, and precipitating the solution with alcohol. After twelve hours the greater portion of the saligenin has crystallized out, and the remainder is extracted from the solution with ether. The crude product is then re-crystallized from hot benzene.[1]

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[1] *Ann. Chem. Pharm.* lvi. 37.

[2] Beilstein and Reineke, *ibid.* cxxviii. 179.

[3] *Amer. Chem. Journ.* ii. 19.

Orthohydroxybenzyl alcohol dissolves in 15 parts of water at 22°, and in almost all proportions in boiling water, readily in alcohol and ether. It crystallizes in small rhombohedra, or tablets, which melt at 82° and sublime at 100°. It forms a bluish red solution in sulphuric acid, and its aqueous solution is coloured deep blue by ferric chloride.

Saliretin, $C_{14}H_{14}O_3 = C_6H_4(OH)CH_2O.C_6H_4.CH_2OH$. Braconnot found that concentrated sulphuric acid converts salicin into a resinous substance, and Piria, who observed that dilute acids have the same effect, gave the product its name, which is intended to suggest both its nature and source.[2]

Saliretin is formed from salicin by elimination of the elements of water; in order to prepare it, salicin is heated to 80° with 10 parts of fuming hydrochloric acid, the product precipitated by water, dissolved in dilute alcohol and again precipitated by a solution of salt.[3]

It is a yellowish powder, which dissolves in alkalis and does not yield either salicylaldehyde or salicylic acid on oxidation. Concentrated nitric acid converts it into picric acid.

The saliretin obtained by the action of concentrated sulphuric acid has the formula $C_{28}H_{26}O_5$,[4] while a compound, $C_{56}H_{50}O_9$, is formed by heating saligenin with acetic anhydride (Beilstein and Seelheim).

Saliretou, $C_{14}H_{12}O_3$, is formed in small quantity, together with other resinous products, when saligenin is heated with glycerol. It crystallizes from hot water in plates or needles, which melt at 121·5°, are coloured red by strong sulphuric acid, and are not affected by ferric chloride.[5]

Orthohydroxybenzyl methyl ether, or *Orthomethoxybenzyl alcohol*, $C_6H_4(OCH_3)CH_2OH$, is formed when saligenin is heated with methyl iodide, caustic potash and wood spirit; it is a liquid, which boils at 247·5° and solidifies in a mixture of ether and solid carbonic acid to a glassy mass.[6]

Orthohydroxybenzyl ethyl ether, $C_6H_4(OC_2H_5)CH_2.OH$, is a pleasant smelling liquid, which boils at 265° and solidifies at 0°

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[1] Beilstein and Seelheim, *Amer. Chem. Journ.* cxvii. 84.
[2] *Ann. Chem. Pharm.* xxx. 179.
[3] Kraut, *ibid.* clvi. 124.
[4] Gerhardt, *Ann. Chim. Phys.* [3] vii. 215.
[5] Giacosa, *Journ. Prakt. Chem.* [2] xxi. 221.
[6] Cannizzaro and Körner, *Ber. Deutsch. Chem Ges.* v. 436.

to a crystalline mass. It gives no colouration with ferric chloride, and is oxidized by dilute nitric acid to ethoxybenzoic acid or ethyl salicylic acid, $C_6H_4(OC_2H_5)CO.OH$.[1]

Caffeol, $C_8H_{10}O_2$. When coffee beans are roasted, the following substances are given off from 100 parts: 0·05 of caffeol, 0·18 of caffeine, 0·48 of fatty acids, chiefly palmitic and acetic, carbon dioxide and small quantities of pyrrol, methylamine and quinol, derived probably from the quinic acid which is contained in the beans.

Caffeol is a liquid which boils at 195°—197°, and possesses the fine aroma of coffee in a very marked degree. Its alcoholic solution gives with ferric chloride a red colouration which is not destroyed by sodium carbonate. It only dissolves with difficulty in concentrated caustic potash solution, and on fusion with caustic potash yields salicylic acid; it is probably therefore a methyl ether of saligenin, and has the constitution $C_6H_4(OH)CH_2.OCH_3$.[2] The fact that it gives a red colouration with ferric chloride, which shows it to be a phenol, is in accordance with this supposition. Rötsch has also found that hydroxybenzyl methyl ether, already mentioned, which is isomeric with caffeol, smells strongly of burnt coffee, but loses the smell completely on purification. This behaviour may be explained by the formation of small quantities of caffeol as a by-product, to which the crude product owes its smell.

2162 *Salicin*, or *Orthohydroxybenzyl glucoside*, $C_6H_4(CH_2.OH)OC_6H_{11}O_5$. After several chemists had unsuccessfully endeavoured to obtain the bitter principle of willow-bark, which was recommended in cases of intermittent fever as a substitute for quinine, in the pure state, Leroux succeeded in purifying it to such an extent that it could be readily crystallized.[3] It was at first thought to be an alkaloid, although this was afterwards shown not to be the case, and the difficulty experienced in obtaining compounds of it with other substances prevented chemists from examining it more closely until Piria subjected it to a careful investigation, which resulted in a complete explanation of its nature.[4]

It occurs in the bark, leaves, and female flowers of many trees which do not all belong to the willow tribe, and to the extent of 4 per cent. in *Salix helix*, *pentandra*, and *præcox*; it has also been found in the bark and leaves of the poplar,[1] in the flower buds of *Spiræa Ulmaria* (p. 286) and in *castoreum*[2] (Wöhler).

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[1] Rötsch, *Monatsch. Chem.* i. 621.

[2] Bernheimer, *ibid.* i. 456.

[3] *Ann. Chim. Phys.* xliii. 440.

[4] *Ann. Chem. Pharm.* xxx. 151 and 189; lvi. 49; Liebig, *ibid.* xxx. 185.

In order to prepare it, 3 parts of willow-bark are extracted three times with boiling water, the extract evaporated down to 9 parts, digested for twenty-four hours with 1 part of litharge, filtered and evaporated to a syrup. The salicin separates out and is purified by re-crystallization.[3] It forms needles, plates, or rhombic prisms, which dissolve in 30 parts of water at the ordinary temperature, and freely in hot water and alcohol, but are insoluble in ether; it has a very bitter taste, and forms a purple-red solution in sulphuric acid. Dilute nitric acid oxidizes it to helicin, $C_6H_4(CHO)OC_6H_{11}O_5$ (p. 288), which may be reconverted into salicin by sodium amalgam and water. As helicin can be artificially prepared by the action of acetochlorohydrose on salicyl aldehyde, it is also possible, as Michael has shown, to prepare salicin artificially; this is the first instance of the synthesis of a glucoside occurring in nature.[4]

Salicin melts at 201°, and solidifies on cooling to a crystalline mass; when it is heated, however, for some time to 230°—240°, it partially decomposes into saliretin and glucosane[5] (Part II. p. 540). Its aqueous solution rotates the plane of polarization to the left.[6] When taken internally a portion of it appears in the urine as saligenin, salicylaldehyde and salicylic acid, the remainder being excreted unchanged;[7] its occurrence in castoreum is thus explained. It is used in medicine in cases of intermittent fever, acute rheumatism, &c., and is also employed for adulterating quinine.

Populin, or *Benzoylsalicin*, $C_{13}H_{17}(C_6H_5.CO)O_7 + 2H_2O$, was discovered by Braconnot in the bark and leaves of the aspen poplar, *Populus tremula*,[8] and carefully investigated by Piria.[9] Piccard also observed it, along with salicin and other substances, in the buds of *Populus pyramidalis, nigra et balsamifera*,[10] and Schiff obtained it artificially by fusing salicin with benzoic anhydride.[11]

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[1] Braconnot, *Ann. Chim. Phys.* xliv. 296; Tischhausen, *Ann. Chem. Pharm.* vii. 280.

[2] *Ibid.* lxvii. 360.

[3] Duflos, *ibid.* viii. 200.

[4] *Amer. Chem. Journ.* v. 171.

[5] Schiff, *Ber. Deutsch. Chem. Ges.* xiv. 304.

[6] Hesse, *Ann. Chem. Pharm.* clxxvi. 116.

[7] Laveran and Millon, *ibid.* lii. 435; Ranke, *Jahresb. Chem.* 1852, 711.

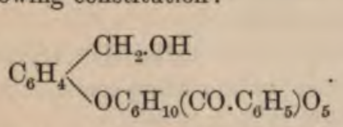
[8] *Ann. Chim. Phys.* xliv. 296.

[9] *Ann. Chem. Pharm.* lxxxi. 245; xcvi. 375.

[10] *Ber. Deutsch. Chem. Ges.* vi. 890.

[11] *Ann. Chem. Pharm.* cliv. 5.

It crystallizes in extremely thin needles, which dissolve in 2,420 parts of water at 15° and in 42 parts at 100°; it loses its water of crystallization at 100° and melts at 180°. Its taste resembles that of liquorice; it is coloured amaranthine red by sulphuric acid. Boiling baryta water decomposes it into salicin and benzoic acid; emulsin has no action upon it, but on boiling with a dilute acid it yields saliretin, benzoic acid and dextrose,[1] while salicin, benzamide, and ethyl benzoate are obtained by heating it with alcoholic ammonia. Nitric acid oxidizes it to benzoyl-helicin, which is the corresponding aldehyde. It has, therefore, the following constitution:



$$C_6H_4\begin{cases} CH_2.OH \\ OC_6H_{10}(CO.C_6H_5)O_5 \end{cases}.$$

2163 *Metahydroxybenzyl alcohol* is obtained by the action of sodium amalgam on an aqueous solution of metahydroxybenzoic acid which is kept acid by the repeated addition of small quantities of hydrochloric acid. It is readily soluble in alcohol and hot water, crystallizes in tough needles, melts at 63°, and boils with partial decomposition at about 300°; its aqueous solution is coloured violet-blue by ferric chloride. Hydrochloric acid converts it into a viscid resin, and on fusion with caustic potash it is oxidized to metahydroxybenzoic acid.

Metahydroxybenzyl acetate, $C_6H_4(OH)CH_2.O.C_2H_3O$, is formed by the action of a mixture of acetic and sulphuric acids on the alcohol, and forms crystals which melt at 55° and are only very slightly soluble in water; the solution is coloured violet-blue by ferric chloride. It boils with decomposition at 295°—302°.

Metahydroxybenzyl diacetate, or *Meta-acetobenzyl acetate*, $C_6H_4(OC_2H_3O)CH_2.OC_2H_3O$, is formed by heating the alcohol to 160° with acetic anhydride, and is a liquid which boils at 290°, and does not give a colouration with ferric chloride.[2]

Parahydroxybenzyl alcohol is obtained by the action of sodium amalgam on a solution of parabenzaldehyde in dilute alcohol acidified with sulphuric acid. It is readily soluble in water, alcohol and ether, and crystallizes in needles, melting at 110°. It forms a splendid reddish violet solution in concentrated sulphuric acid.[3]

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[1] Schmidt, *Ann. Chem. Pharm.* xix. 92.
[2] Velden, *Journ. Prakt. Chem.* [2] xv. 165.
[3] Biedermann, *Ber. Deutsch. Chem. Ges.* xix. 2373.

Parahydroxybenzyl methyl ether, or *Anise alcohol*, $C_6H_4(OCH_3)CH_2.OH$, is formed by the action of alcoholic potash on anisaldehyde (paramethoxybenzaldehyde).[1] It is also formed when parahydroxybenzyl alcohol is heated with methyl iodide and caustic potash, and crystallizes in hard, lustrous needles, which have a faint spirituous odour and a burning taste; it melts at 25°, and boils at 258·8°.[2]

Paramethoxybenzyl chloride, $C_6H_4(OCH_3)CH_2Cl$, is prepared by saturating the alcohol with hydrochloric acid; it is a liquid with a fruity odour and burning taste. On treatment with sodium methylate it yields the dimethyl ether $C_6H_4(OCH_3)CH_2.OCH_3$, a liquid boiling at 225·5°.[3]

Parahydroxybenzyl acetate, $C_6H_4(OH)CH_2.O.C_2H_3O$, is formed in a similar manner to the meta-compound, and crystallizes in yellowish needles melting at 84°.

Para-acetobenzyl acetate, $C_6H_4(OC_2H_3O)CH_2.OC_2H_3O$, also forms yellow needles, melting at 75° (Biedermann).

Paramethoxybenzylamine, $C_6H_4(OCH_3)CH_2.NH_2$, is obtained by the action of ammonia on the chloride, and crystallizes from hot water in small needles which have a strongly alkaline reaction and melt above 100°. The secondary base, $(C_8H_9O)_2NH$, is formed simultaneously; it is less soluble in water, and crystallizes in plates melting at 32°—33°.[4]

Parahydroxybenzyl thiocarbimide, $C_6H_4(OH)CH_2.N = CS$, has been already mentioned as sinalbin mustard oil (Part II. p. 392). It is a product of the decomposition of sinalbin, $C_{30}H_{44}N_2S_2O_{16}$, which crystallizes in small, lustrous needles and is readily soluble in water, slightly in alcohol; it is converted by myrosin in presence of water into sinalbin mustard oil, acid sinapin sulphate, and grape sugar:

$$C_{30}H_{44}N_2S_2O_{16} = C_8H_7NOS + C_{16}H_{23}NO_5.H_2SO_4 + C_6H_{12}O_6.$$

Sinalbin mustard oil is a non-volatile, oily liquid, which has a very sharp taste and blisters the skin. When the sulphur is removed it is converted into *parahydroxyphenylacetonitril*, $C_6H_4(OH)CH_2.CN$, which was considered to be the ortho-compound by Laubenheimer and Will.[5]

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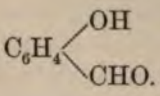
[1] Bertagnini and Cannizzaro, *Ann. Chem. Pharm.* xcviii. 189.
[2] Cannizzaro and Körner, *Ber. Deutsch. Chem. Ges.* v. 436.
[3] Cannizzaro, *Ann. Chem. Pharm.* cxxxvii. 246.
[4] *Ibid.* cxvii. 240.
[5] *Ann. Chem. Pharm.* cxcix. 150.

HYDROXYBENZALDEHYDES,



$C_6H_4\left\langle\begin{matrix}OH\\CHO\end{matrix}\right.$

ORTHOHYDROXYBENZALDEHYDE, OR SALICYLALDEHYDE.

2164 The volatile oil of the flowers of *Spiræa Ulmaria* was first examined by Pagenstecher, an apothecary of Berne, who discovered in it an acid, the aqueous solution of which is coloured violet by ferric chloride,[1] and which was called "*spiroylwasserstoffsäure*," $C_{12}H_6O(C=6,O=8)$ by Löwig, to whom Pagenstecher intrusted its further investigation.[2] He and Weidmann subsequently found that when the ethereal solution is shaken with caustic potash, this is coloured yellow, and on evaporation of the ether an indifferent oil remains behind, which possesses the smell of the flowers in a very marked degree, while if the alkaline solution be distilled with phosphoric acid, an acid oil passes over first, followed by an acid crystallizing in long needles. They now called the former of these *spiræic acid*, or *spiroyl hydride*, $C_{13}H_{10}O_4$.[3] About the same time, Piria, working in Dumas' laboratory, found that salicin on oxidation with potassium dichromate and dilute sulphuric acid yields a volatile, oily, aromatic liquid, which he called *salicyl hydride*, $C_7H_6O_2$. This is isomeric with benzoic acid, and is to be looked upon as a hydracid, which, on heating with caustic potash, yields salicylic acid, $C_7H_6O_3$, just as benzoyl hydride under similar circumstances yields benzoic acid. The radicals *benzoyl*, C_7H_5O, and *salicyl*, $C_7H_5O_2$, are different oxidation products of the hydrocarbon, C_7H_5.[4] Dumas, to whom Pagenstecher showed his preparations from Spiræa, noticed the great similarity of the oil to salicyl hydride and suggested that spiræic acid is identical with the latter;[5] this had already been proved by Ettling, who named the compound salicylous or spiroylous acid.[6]

The compound was mistaken for an acid because it is at once an aldehyde and a phenol, and therefore forms salts.

Salicylaldehyde also occurs in the juice of various plants belonging to the genus Spiræa,[1] in the stem and root of *Crepis fœtida*,[2] and in the larvæ of *Chrysomela populi*, which live on willows and poplars, and possess small openings along the body from which salicyl aldehyde may be pressed out in oily drops.[3] Enz also obtained it by distilling the beetle with water.[4]

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[1] Buchner's *Repert. Pharm.* xlix. 337 ; li. 364.
[2] *Pogg. Ann.* xxxvi. 383.
[3] *Ibid.* xlvi. 57.
[4] *Ann. Chem. Pharm.* xxix. 300, xxx. 151.
[5] *Ibid.* xxix. 306.
[6] *Ibid.* xxix. 309 ; xxxv. 241.

In order to prepare it, a mixture of 3 parts of salicin and 3 parts of potassium dichromate is treated with 24 parts of water, to which 4·5 parts of sulphuric acid diluted with 12 parts of water are added. When the reaction is complete, the mixture is distilled until the distillate passes over clear, and the oily portion then separated from the water; some of the aldehyde remains dissolved in the water and is extracted by ether.[5]

If the distillation be continued too long, furfurol passes over, and all preparations made from the aldehyde then become intensely red-coloured on standing.[6]

The flower-buds of *Spiræa Ulmaria* only give a very small yield of salicyl aldehyde on distillation with water, but a larger quantity is obtained when sulphuric acid and potassium dichromate are added, thus showing that the buds contain salicin.[7] Salicyl aldehyde is obtained synthetically, along with the isomeric parahydroxybenzaldehyde, by the action of chloroform on a solution of phenol in caustic soda (Part III. p. 32). They are separated by distillation in steam, with which the latter is not volatile.[8]

Properties.—Salicylaldehyde is a liquid with a pleasant aromatic smell and a burning spice-like taste; it boils at 196·5°, solidifies at 20° to large crystals, and has a specific gravity of 1·1731 at 13·5°. Its aqueous solution, even when very dilute, is coloured violet by ferric chloride, and yellow by alkalis; it does not reduce Fehling's solution,[9] and forms difficultly soluble compounds with the acid sulphites of the alkali metals,[10] this property being made use of in its purification (Reimer and Tiemann). It produces a fine reddish violet colouration in a solution of rosaniline which has been decolourized by sulphurous acid.[11] The aldehydes of the fatty acids, benzaldehyde, &c., also give this reaction (Part II. p. 495).

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[1] Wicke, *Ann. Chem. Pharm.* lxxxiii. 175.

[2] *Ibid.* xci. 374.

[3] *Jahresber. Chem.* 1850, 583.

[4] *Ibid.* 1859, 312.

[5] Schiff, *Ann. Chem. Pharm.* cl. 193.

[6] *Ibid.* ccx. 115.

[7] Buchner, *ibid.* lxxxviii. 284.

[8] Reimer and Tiemann, *Ber. Deutsch. Chem. Ges.* ix. 824.

[9] Tollens, *ibid.* xiv. 1959.

[10] Bertagnini, *Ann. Chem. Pharm.* lxxxv. 93.

[11] Schmidt, *Ber. Deutsch. Chem. Ges.* xiv. 1848.

As a phenol it forms salts, ethers, and ethereal salts.

Potassium salicylaldehyde, $C_6H_4(OK)CHO + H_2O$, is obtained by adding caustic potash to a solution of the aldehyde in dilute alcohol; it crystallizes in light yellow, nacreous, quadratic tablets, which are readily soluble in water. The compound $C_6H_4(OK)CHO + C_6H_4(OH)CHO$ is obtained in fine, fascicular groups of needles by adding the aldehyde to an alcoholic solution of the potassium salt.

Barium salicylaldehyde, $(C_6H_4(CHO)O)_2Ba + 2H_2O$, crystallizes in yellow needles, which are slightly soluble in cold water.

Copper salicylaldehyde, $(C_6H_4(CHO)O)_2Cu$, is a very characteristic salt; when an aqueous solution of copper acetate is added to a dilute alcoholic solution of the aldehyde, the liquid becomes coloured emerald green, and after a few minutes deposits sparkling crystals; the liquid then presents a most beautiful appearance when placed in the sunlight. The crystals become brownish-green on drying, and are only slightly soluble in water and alcohol (Ettling).

Lead salicylaldehyde, $C_6H_4(CHO)OPb.OH$, is formed when basic lead acetate is added to an alcoholic solution of the aldehyde; it is a yellow precipitate which dissolves on heating, and separates out on cooling in heavy, light-yellow granules.

Methyl salicylaldehyde, $C_6H_4(OCH_3)CHO$, is obtained by heating the sodium salt with methyl alcohol and methyl iodide.[1] It is an oily liquid which possesses a faint odour, boils at 238°, and, when perfectly free from salicylaldehyde, solidifies after some time to tough prisms melting at 35°. It forms a compound with acid ammonium sulphite, which crystallizes in lustrous prisms and is readily soluble in water and alcohol. The potassium sulphite compound also crystallizes well, but is only slightly soluble in cold alcohol.

Ethyl salicylaldehyde, $C_6H_4(OC_2H_5)CHO$, was obtained by Perkin in a similar manner, as a strongly refractive liquid boiling at 247°—249°. It is also formed when a mixture of calcium formate and calcium ethyl salicylate is distilled, while, when calcium salicylate is substituted for the ethyl compound, only phenol is formed.[2]

Benzyl salicylaldehyde, $C_6H_4(OCH_2.C_6H_5)CHO$, crystallizes from boiling alcohol in flat, rhombic prisms, which melt at 46°, and have a faint odour resembling that of cloves. It boils above 360°, and forms an irritating vapour.[1]

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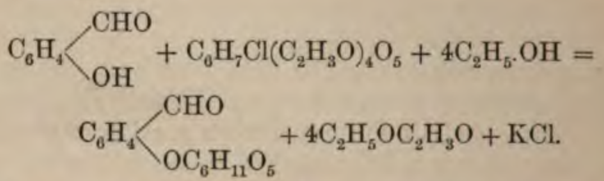
[1] Perkin, *Journ. Chem. Soc.* xx. 418; Voswinkel, *Ber. Deutsch. Chem. Ges.* xv. 2024.

[2] Göttig, *ibid.* x. 8.

Acetyl salicylaldehyde, $C_6H_4(OC_2H_3O)CHO$, is formed when the sodium salt is suspended in ether and treated with acetic anhydride. It is extremely soluble in alcohol, crystallizes in fine, silky needles, melts at 37°, and then solidifies to a mass possessing a satin lustre. Its boiling-point lies at about 253°; it combines with the acid sulphites of the alkali metals.[2]

Benzoyl salicylaldehyde, $C_6H_4(O.CO.C_6H_5)CHO$, was obtained by Perkin by the action of benzoyl chloride on the sodium compound. It is a thick oily liquid, which boils above 360°, and forms the usual compounds with the acid sulphites of the alkali metals.[3]

2165 *Helicin*, $4C_6H_4(OC_6H_{11}O_5)CHO + 3H_2O$, is formed by the action of dilute nitric acid on salicin.[4] In order to prepare it, salicin is treated in flat basins or plates with eight times its weight of nitric acid of sp. gr. 1·15, containing lower oxides of nitrogen, which may be introduced by the addition of a few drops of the red, fuming acid. The helicin is filtered off after some hours and washed two or three times with cold water.[5] It is readily soluble in hot water and alcohol, but not in ether, and crystallizes in small, very fine needles, which have a faint, bitter taste, lose their water of crystallization at 100° and melt at 175°. It is not coloured by ferric chloride; if a blood-red colouration be produced, it contains nitrosalicylic acid. It is resolved into dextrose and salicylaldehyde by the action of acids, alkalis and emulsin. It can be synthetically prepared by acting upon potassium salicylaldehyde with an alcoholic solution of acetochlorohydrose:[6]



$$C_6H_4\left\langle\begin{matrix}CHO\\OH\end{matrix}\right. + C_6H_7Cl(C_2H_3O)_4O_5 + 4C_2H_5.OH =$$
$$C_6H_4\left\langle\begin{matrix}CHO\\OC_6H_{11}O_5\end{matrix}\right. + 4C_2H_5OC_2H_3O + KCl.$$

It is reduced to salicin by the action of sodium amalgam and water.[7] It forms a compound with acid sodium sulphite, which has the formula $C_{13}H_{16}O_7.SO_3HNa$, and forms a dazzling white, hygroscopic, crystalline mass.[1]

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[1] Perkin, *Journ. Chem. Soc.* xxi. 122.

[2] *Ibid.* xxi. 181.

[3] *Ibid.* cxlv. 295.

[4] Piria, *ibid.* lvi. 64.

[5] Schiff, *ibid.* cliv. 14.

[6] Michael, *Amer. Chem. Journ.* i. 309.

[7] Lisenko, *Jahresber. Chem.* 1864, 588.

When it is moistened with one per cent. nitric acid, dried and heated to 110°—115°, it is converted into parahelicin, which is without doubt a polymeride; this substance is an amorphous, starchy, tasteless powder, which is scarcely soluble in water and alcohol, and has no action upon a solution of rosaniline reduced by sulphurous acid, whereas helicin forms a reddish violet crystalline compound with it. It dissolves in very dilute hydrochloric acid which has been slightly warmed, and is thus reconverted into helicin.[2]

Tetracetylhelicin, $C_{13}H_{12}(C_2H_3O)_4$, was obtained by Schiff by heating helicin with acetyl chloride or acetic anhydride; it crystallizes from hot alcohol in long, silky needles or prisms.

Benzoylhelicin, $C_{13}H_{15}(CO.C_6H_5)O_7$. Piria prepared this compound by the action of nitric acid on populin (p. 282),[3] and Schiff by heating helicin with benzoyl chloride.[4] It crystallizes in silky needles, which are slightly soluble in water, more readily in alcohol. Sodium amalgam and water reduce it again to populin; on boiling with water and magnesia it is decomposed into helicin and benzoic acid.

Helicoïdin, $C_{26}H_{34}O_{14}$, is formed by dissolving salicin in nitric acid of sp. gr. 1·085 :

$$2C_{13}H_{18}O_7 + O = C_{26}H_{34}O_{14} + H_2O.$$

It crystallizes from hot water in needles, and is very similar to helicin, from which it differs in being resolved by acids, &c., into dextrose, salicylaldehyde, and saligenin (Piria).

Octacetylhelicoïdin, $C_{26}H_{26}(C_2H_3O)_8O_{14}$, is obtained by heating helicoïdin to 100° with acetic anhydride; it is insoluble in water, and crystallizes from alcohol in druse-like aggregates, melting at 80° (Schiff).

Ortho-aldehydophenoxyacetic acid, $C_6H_4(COH)OCH_2.CO_2H$, is formed when equal molecules of salicylaldehyde and chloracetic acid are heated together and the fused mass treated with an excess of caustic soda solution of sp. gr. 1·2—1·3; the mixture is then heated on the water-bath until it has become almost solid, the acid precipitated by hydrochloric acid and re-crystallised from hot water. It forms large, yellow plates, which melt at 132°, and sublime when gradually heated. Like other aldehydes it reduces Fehling's solution and ammoniacal silver solution, and combines with phenylhydrazine and acid sodium sulphite. Its salts are readily soluble and crystallise well; its ethyl ether forms needles melting at 114°.[1]

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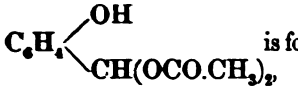
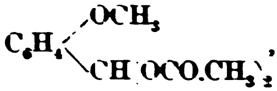
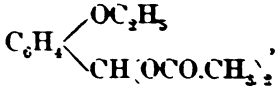
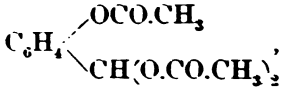
[1] Schiff, *Ann. Chem. Pharm.* ccx. 126.
[2] *Ibid. Ber. Deutsch. Chem. Ges.* xiv. 317.
[3] *Ann. Chem. Pharm.* xcvi. 379.
[4] *Ibid.* cliv. 23.

2166 *Orthohydroxybenzidene compounds.* These are obtained in a similar manner to the benzidene compounds.

Orthohydroxybenzidene acetate,  $C_6H_4\begin{cases}OH\\CH(OCO.CH_3)_2\end{cases}$ is formed when salicylaldehyde is heated to 150° with acetic anhydride; it crystallises from alcohol in thick, hard, transparent tablets, which melt at 103°—104°, and distil with slight decomposition.[2]

Perkin has obtained the following compounds in a similar manner:

		Melting-point.
 $C_6H_4\begin{cases}OCH_3\\CH(OCO.CH_3)_2\end{cases}$	, lustrous prisms	75°
 $C_6H_4\begin{cases}OC_2H_5\\CH(OCO.CH_3)_2\end{cases}$	, small prisms	88°—89°
 $C_6H_4\begin{cases}OCO.CH_3\\CH(O.CO.CH_3)_2\end{cases}$	, needles or pointed tablets	100°—101°

The last compound may also be obtained by heating salicylaldehyde to 180° with acetic anhydride.[3] Tolerably concentrated caustic potash decomposes it into acetic acid and orthohydroxybenzidene acetate, while it splits up on distillation into acetylsalicylaldehyde and acetic anhydride.[4]

Orthohydroxybenzidenoxime, or *Salicylaldoxime*, $C_6H_4(OH)CH{=}N.OH$, is formed by the action of hydroxylamine on salicylaldehyde, and forms white crystals which dissolve readily in alcohol, ether and benzene, but are insoluble in petroleum spirit, and melt at 57°.[5] Its compounds resemble those of benzaldoxime (p. 139).

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[1] Rössing, *Ber. Deutsch. Chem. Ges.* xvii. 2988.
[2] Perkin, *Ann. Chem. Pharm.* cxlvi. 371.
[3] Barbier, *Bull. Soc. Chim.* xxxiii. 53.
[4] Perkin, *Ann. Chem. Pharm.* cxlviii. 203.
[5] Lach, *Ber. Deutsch. Chem. Ges.* xvi. 1782.

Hydroxybenzidene-amidobenzoic acid, $C_6H_4(OH)CH{=}NC_6H_4CO_2H$, is prepared by mixing warm, dilute, aqueous solutions of salicylaldehyde and metamidobenzoic acid. It crystallizes in long, yellow needles, which are very soluble in alcohol and benzene. Its aqueous solution gives off salicylaldehyde on evaporation.[1]

Helicin combines with metamidobenzoic acid to form the analogous compound $C_6H_4(OC_6H_{11}O_5)CH{=}NC_6H_4.CO_2H$, which crystallizes from alcohol in lustrous plates, melting at 142°;[2] it is resolved into the preceding compound and grape sugar by heating with an aqueous solution of emulsin.

Hydrosalicylamide, $N_2(CH.C_6H_4.OH)_3$. This compound, corresponding to hydrobenzamide (p. 140), was prepared by Ettling by the action of ammonia on an alcoholic solution of salicylaldehyde, and named by him salicylimide.[3] It forms heavy, light yellow crystals, melting at 300°, and is insoluble in water, slightly in cold, more readily in hot alcohol, and decomposes into salicylaldehyde and ammonia when heated with concentrated caustic potash solution or strong acids. It absorbs three molecules of hydrochloric acid, forming a compound which decomposes in moist air into salicylaldehyde and ammonium chloride.[4]

As a phenol it forms metallic salts; when an ammoniacal solution of copper acetate is added to its cold alcoholic solution, the liquid becomes coloured emerald-green, and after a few minutes becomes decolourized, cruciform plates being deposited, which after drying have a strong satin lustre; their composition is represented by the formula $(C_{21}H_{15}N_2O_3)_2Cu_3(NH_3)_2$. They are almost insoluble in water and alcohol, and form a green solution in hydrochloric acid, from which they are reprecipitated by alkalis. They are not attacked by cold caustic potash, and decomposition only proceeds slowly on boiling; salicylaldehyde is formed when it is heated with strong acids.

Orthobenzidenephenylhydrazine, $C_6H_4(OH)CH{=}N_2H.C_6H_5$, crystallizes from hot, dilute alcohol in yellow needles or plates, melting at 142°—143°. When it is heated with chloracetic acid a colouring matter, $C_9H_7NO_3$, is produced, which forms a deep bluish green solution in alcohol and is coloured cherry-red by alkalis.[5]

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[1] Schiff, *Ann. Chem. Pharm.* ccx. 114.
[2] *Ber. Deutsch. Chem. Ges.* xii. 2032.
[3] *Ann. Chem. Pharm.* xxxv. 261.
[4] Bodo, *Jahresb. Chem.* 1857, 318.
[5] Fischer, *Ber. Deutsch. Chem. Ges.* xvii. 575; Rössing, *ibid.* 3004.

SUBSTITUTION PRODUCTS OF SALICYLALDEHYDE.

2167 *Chlorosalicylaldehyde*, $C_6H_3Cl(OH)CHO$, is formed by the action of chlorine on salicylaldehyde.[1] It is insoluble in water, and crystallizes from alcohol in rectangular tablets.

Bromosalicylaldehyde, $C_6H_3Br(OH)CHO$, is not only formed by the direct action of bromine[2] but also when salicylaldehyde is treated with phosphorus pentabromide, the latter compound acting in the same manner as a mixture of bromine and phosphorus pentabromide.[3] It crystallizes from ether in small plates, melting at 98°—99°; its alcoholic solution is coloured violet by ferric chloride.

	Melting-point
Methylbromosalicylaldehyde, flat prisms $C_6H_3Br(OCH_3)CHO$.	113°—114·5°.
Ethylbromosalicylaldehyde,[4] sharp prisms $C_6H_3Br(OC_2H_5)CHO$.	67°—68°.

a-Nitrosalicylaldehyde, $C_6H_3(NO_2)(OH)CHO$, is formed, together with the β-compound, by boiling salicylaldehyde with dilute nitric acid;[5] the two substances are separated by means of their barium salts. *a*-Nitrosalicylaldehyde crystallizes in small yellow prisms, which melt at 105°—107°, while its barium salt, $(C_7H_4NO_4)_2Ba + 2H_2O$, forms slightly soluble, yellowish red columns.

β-Nitrosalicylaldehyde forms needles, melting at 123°—125°; its barium salt, $(C_7H_4NO_4)_2Ba + 6H_2O$, crystallizes in yellow prisms.

Methylnitrosalicylaldehyde, $C_6H_3(NO_2)(OCH_3)CHO$, forms fine, white needles, melting at 85°.[6]

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[1] Piria, *Ann. Chem. Pharm.* xxx. 169; Löwig, *Berz. Jahresb.* xx. 311.

[2] Piria; Löwig, *Pogg. Ann.* xlvi. 57; Heberlein, *Berz. Jahresb.* xxv. 484.

[3] Henry, *Ber. Deutsch. Chem. Ges.* ii. 274.

[4] Perkin, *Ann. Chem. Pharm.* cxlv. 304.

[5] Mazzara, *Gazz. Chim. Ital.* vi. 460.

[6] Voswinkel, *Ber. Deutsch. Chem. Ges.* xv. 2027; Schnell, *ibid.* xvii. 1381.

METAHYDROXYBENZALDEHYDE.

2168 This compound is formed, together with metahydroxybenzyl alcohol, by the action of sodium amalgam on a faintly acid solution of metahydroxybenzoic acid. It can be more readily obtained from metamidobenzaldehyde by treating its well-cooled solution in hydrochloric acid with the calculated quantity of sodium nitrite and then heating.[1] It crystallizes from hot water in white needles, melting at 104°; its aqueous solution is coloured a faint violet by ferric chloride, and it differs from the isomeric para-compound in giving a precipitate with lead acetate.

Methylmetahydroxybenzaldehyde, $C_6H_4(OCH_3)CHO$, is obtained by heating the aldehyde with caustic potash, methyl iodide and wood-spirit. It is an oily liquid, which boils at 230° and has a pleasant odour.

Acetylmetahydroxybenzaldehyde, $C_6H_4(OCO.CH_3)CHO$, is formed by the action of acetic anhydride on the potassium compound of the aldehyde, and is an oily liquid, boiling at 263.°

Acetometahydroxybenzidene acetate, $C_6H_4(OCO.CH_3)CH(O.CO.CH_3)_2$, is produced when the aldehyde is boiled with an excess of acetic anhydride. It is slightly soluble in water, readily in alcohol, and crystallizes in lustrous, white plates, melting at 76.°

Nitro-substitution products. The three following compounds are all formed by the direct nitration of the aldehyde; they may be separated by re-crystallization from hot water, chloroform, &c.

α-Nitrometahydroxybenzaldehyde, $C_6H_3(NO_2)(OH)CHO$, crystallizes in yellowish plates, melting at 128°, which are slightly soluble in cold, more readily in hot water, and readily in chloroform and petroleum ether.

β-Nitrometahydroxybenzaldehyde forms needles which melt at 166°, and is more readily soluble in water than the *α*-compound, but only very slightly soluble in chloroform and benzene.

γ-Nitrometahydroxybenzaldehyde melts at 138°, and crystallizes in prisms, which dissolve readily in hot water, chloroform and benzene, but only with difficulty in petroleum ether.

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[1] Tiemann and Ludwig, *Ber. Deutsch. Chem. Ges.* xv. 2043 and 3052.

When these compounds are heated with caustic potash, wood-spirit and methyl iodide, their methyl ethers, $C_6H_3(NO_2)(OCH_3)CHO$, are formed (Tiemann and Ludwig); these can also be obtained by the nitration of metamethoxybenzaldehyde.[1]

α-Orthonitromethylmetahydroxybenzaldehyde crystallizes from chloroform in thick, yellow prisms, melting at 107°.

β-Orthonitromethylmetahydroxybenzaldehyde forms white plates or needles, which melt at 82°—83°.

These bodies are known to be orthonitro-compounds because they give the indigo reaction (p. 146).

Metanitromethylmetahydroxybenzaldehyde crystallizes in needles or prisms, and melts at 98°.

Paranitromethylmetahydroxybenzaldehyde was obtained by Ulrich by the oxidation of paranitromethoxycinnamic acid; it crystallizes in hair-like needles and melts at 62°.

PARAHYDROXYBENZALDEHYDE.

2169 This body was first prepared by Bücking by heating the methyl ether, anisaldehyde, with hydrochloric acid.[2] It may be synthetically obtained by the action of chloroform on an alkaline solution of phenol, salicylaldehyde being formed at the same time.

In order to prepare it, 30 parts of chloroform are gradually added to a solution of 20 parts of phenol in 120 parts of water heated to 50°—60°; the liquid becomes coloured blue and then deep red, a considerable rise of temperature taking place, the use of an inverted condenser being thus rendered necessary. The mixture is finally boiled for half an hour, the excess of chloroform distilled off, an excess of sulphuric acid added, and the whole distilled in steam, salicylaldehyde passing over along with any free phenol, from which it is subsequently separated by means of acid sodium sulphite. The residual liquid is filtered while hot from the deep red coloured resin which is formed, and after cooling is extracted with ether; on evaporation of the ether, the parahydroxybenzaldehyde is left behind, and is then re-crystallized from boiling water.[3] It is slightly soluble in cold, more readily in hot water, and readily in alcohol, ether, &c., and crystallizes in fine needles, which have a faint but pleasant aromatic odour, melt at 115°—116°, and sublime unaltered. Its aqueous solution is coloured a dirty violet by ferric chloride; if its ethereal solution be shaken up with a solution of acid sodium sulphite, combination ensues, but the double compound is readily soluble. Its solution is not easily attacked by oxidizing agents, but it is converted into parahydroxybenzoic acid by fusion with caustic potash at a low temperature.

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[1] M. Ulrich, *Ber. Deutsch. Chem. Ges.* xviii. 2571.

[2] *Ibid.* ix. 527.

[3] Reimer and Tiemann, *ibid.* ix. 824; Tiemann and Herzfeld, *ibid.* x. 63.

Methylparahydroxybenzaldehyde, $C_6H_4(OCH_3)CHO$. Cahours prepared this compound by the oxidation of oil of anise seed,[1] while Cannizzaro and Bertagnini obtained it by oxidizing anise alcohol (p. 284), and named it anisaldehyde.[2] Piria then showed that it is also formed by distilling a mixture of calcium formate and calcium anisate (methylparahydroxybenzoate);[3] and Tiemann and Herzfeld obtained it by heating parahydroxybenzaldehyde with methyl iodide, wood spirit and caustic potash.

It may be most readily prepared from oil of anise, which consists for the most part of anethol, $C_3H_5.C_6H_5.OCH_3$, the methyl ether of allylphenol. One part of this is brought into a cold solution of 2 parts of potassium dichromate, 3 parts of sulphuric acid, and 8 parts of water. As soon as the temperature ceases to rise, the mixture is diluted with half its volume of water and distilled, the quantity of liquid in the distilling flask being kept at its original volume by the gradual addition of water. The distillate is repeatedly rectified, the aldehyde coming over in the first portions, which are then shaken up with a concentrated solution of acid sodium sulphite. The crystals, which separate after some time, are washed with alcohol and decomposed by carbonate of soda solution.[4]

Anisaldehyde is a liquid which has an aromatic odour, boils at 247°—248°, and dissolves slightly in cold, more readily in hot water; it readily takes up oxygen from the air and is converted by alcoholic potash into a mixture of anise alcohol and anisic acid. When heated with dilute hydrochloric acid to 200°, it decomposes into parahydroxybenzaldehyde and methyl chloride (Bücking).

Acetylparahydroxybenzaldehyde, $C_6H_4(OCO.CH_3)CHO$, is obtained by dissolving 2 parts of parahydroxybenzaldehyde and 1 part of caustic potash in water, evaporating and treating the residue with acetic anhydride in presence of ether (Tiemann and Herzfeld).

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[1] *Ann. Chem. Pharm.* lvi. 307.

[2] *Ibid.* xcviii. 189.

[3] *Ibid.* c. 105.

[4] Rossel, *ibid.* cli. 28.

It is also formed by the action of acetic anhydride on the aldehyde,[1] and is a liquid, boiling at 264°—265°, which forms an almost insoluble compound with acid sodium sulphite.

Acetylparahydroxybenzidene acetate, $C_6H_4(OCO.CH_3)CH(OCO.CH_3)_2$, is prepared by heating the aldehyde with three times its weight of acetic anhydride. It is readily soluble in hot water and alcohol, and crystallizes from ether in flat prisms, melting at 93°—94° (Tiemann and Herzfeld).

Parahydroxybenzaldoxime, $C_6H_4(OH)CH{=}NOH$, forms odourless, white needles.[2]

Chloroparahydroxybenzaldehyde, $C_6H_3Cl(OH)CHO$, crystallizes from hot water in silky needles melting at 148°—149°; its aqueous solution is coloured violet by ferric chloride.

Bromoparahydroxybenzaldehyde, $C_6H_3Br(OH)CHO$, is almost insoluble in water, crystallizes from alcohol in long, strongly refractive needles, melting at 179°—180°, and does not give any colouration with ferric chloride.

Iodoparahydroxybenzaldehyde, $C_6H_3I(OH)CHO$, is formed when parahydroxybenzaldehyde is boiled with iodine and dilute alcohol. It is slightly soluble in water, readily in alcohol, and separates from chloroform in white crystals, melting at 198°—199°. On heating with caustic potash it yields protocatechuic acid.[3]

Nitroparahydroxybenzaldehyde, $C_6H_3(NO_2)(OH)CHO$. Mazzara obtained this substance by boiling the aldehyde with dilute sulphuric acid,[4] and Herzfeld by adding concentrated nitric acid to a solution of parahydroxybenzaldehyde in concentrated sulphuric acid.[5] It is soluble in boiling water and alcohol, and crystallizes in yellowish needles melting at 139°—140°. Its aqueous solution gives a fugitive red colouration with ferric chloride. It decomposes carbonates; the potassium salt, $C_6H_3(NO_2)(OK)CHO + H_2O$, forms golden-yellow tablets.

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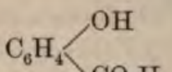
[1] Barbier, *Bull. Soc. Chim.* xxxiii. 54.
[2] Lach, *Ber. Deutsch. Chem. Ges.* xvi. 1785.
[3] Herzfeld, *ibid.* x. 2196.
[4] *Gaz. Chim. Ital.* vii. 285.
[5] *Ber. Deutsch. Chem. Ges.* x. 1269.



HYDROXYBENZOIC ACIDS, $C_6H_4\left\langle\begin{matrix}OH\\CO_2H.\end{matrix}\right.$

ORTHOHYDROXYBENZOIC ACID, OR SALICYLIC ACID.

2170 The history of this important substance is of special interest because its genetic relations to the benzoyl and cinnamyl groups and to indigo blue were known at a very early period. Piria, who prepared it in 1838, by heating the aldehyde with caustic potash,[1] pointed out that the radicals benzoyl and salicyl are different oxidation products of the hydrocarbon or radical C_7H_5 (p. 285). Marchand[2] and Gerhardt[3] found that it is also formed when salicin is melted with potash, and is converted by dilute nitric acid into nitrosalicylic acid, which is identical with indigotic or anilotic acid, a substance obtained by the action of nitric acid on indigo which had long been familiar to chemists. This compound on fusion with potash at a low temperature yields anthranilic acid (p. 237), while Cahours, by carrying out the operation at a higher temperature, obtained salicylic acid;[4] it was obtained, together with acetic acid, in a similar manner from cumaric acid by Delalande, who remarked that this latter compound bears the same relation to cinnamic acid as salicylic to benzoic acid.[5] Ettling, who prepared salicylic acid by oxidizing its aldehyde with potassium dichromate and sulphuric acid, found that it can also be obtained by heating the copper salt of this or of benzoic acid, and is therefore an oxidation product of the latter.[6] Gerhardt had previously observed that salicylic acid decomposes on heating into phenol and carbon dioxide, just as anthranilic acid is split up into aniline and carbon dioxide. A series of relations was thus established among the following compounds:

Benzene	Benzoic acid	Cinnamic acid
C_6H_6	$C_7H_6O_2$	$C_9H_8O_2$
Phenol	Salicylic acid	Cumaric acid
C_6H_6O	$C_7H_6O_3$	$C_9H_8O_3$
Aniline	Anthranilic acid	
C_6H_7N	$C_7H_7NO_2$	—

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[1] *Ann. Chim. Phys.* lxix. 298; *Ann. Chem. Pharm.* xxx. 165.

[2] *Journ. Prakt. Chem.* [1] xxvi. 396.

[3] *Ann. Chem. Pharm.* xlv. 19.

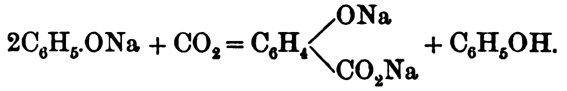
[4] *Ibid.* lii. 343.

[5] *Ibid.* xlv. 336.

[6] *Ibid.* liii. 77.

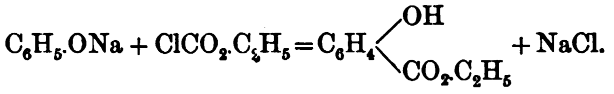
Hofmann found that aniline is converted into phenol by the action of nitrous acid, and suggested that anthranilic acid would probably yield salicylic acid when treated in a similar manner, this suggestion being experimentally verified by Gerland.[1]

Salicylic acid was obtained synthetically by Kolbe and Lautemann by the action of carbon dioxide on a mixture of phenol and sodium.[2] The former chemist found that it is also formed when carbon dioxide is passed over heated sodium phenate, half of the phenol being set free:[3]



$$2C_6H_5.ONa + CO_2 = C_6H_4\begin{cases}ONa\\CO_2Na\end{cases} + C_6H_5OH.$$

Ethyl salicylate may be prepared by the action of sodium on a mixture of phenol and ethyl chloroformate:[4]



$$C_6H_5.ONa + ClCO_2.C_2H_5 = C_6H_4\begin{cases}OH\\CO_2.C_2H_5\end{cases} + NaCl.$$

The acid is also formed, together with parahydroxybenzoic acid, when a mixture of tetrachloromethane and phenol is heated to 100° with alcoholic potash (Part III. p. 32).[5]

It may also be obtained by fusing orthocresol,[6] tolueneorthosulphonic acid,[7] &c., with caustic potash, as well as by heating copper benzoate to 180° with water,[8] and when sodium is allowed to remain in contact with ethyl succinate for a long time.[9] It has also been observed as a product of the action of hydrogen dioxide on a solution of benzoic acid in sulphuric acid.[10]

Salicylic acid also occurs in nature. Löwig and Weidmann detected it in the flowers of *Spiræa Ulmaria*, accompanied by salicylaldehyde, but did not actually identify it. Its methyl ether is contained in the ethereal oils of the various species of *Gaultheria*.

2171 It was formerly prepared exclusively from the winter-green oil obtained from *Gaultheria procumbens* by saponifying with potash and decomposing the product with hydrochloric acid. It is now manufactured by Kolbe's process.

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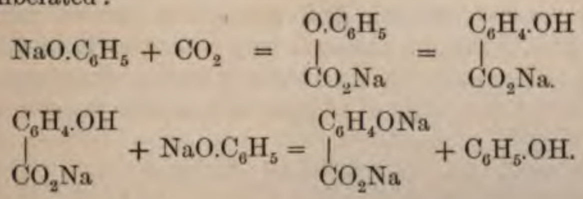
[1] *Ann. Chem. Pharm.* lxxxvi. 147.
[2] *Ibid.* cxv. 201.
[3] *Journ. Prakt. Chem.* [2] x. 89.
[4] Wilm and Wischin, *Zeitschr. Chem.* 1868, 6.
[5] Reimer and Tiemann, *Ber. Deutsch. Chem. Ges.* ix. 1285.
[6] Barth, *Ann. Chem. Pharm.* cliv. 360.
[7] Wolkow, *Zeitschr. Chem.* 1870, 326.
[8] Smith, *Amer. Chem. Journ.* ii. 338.
[9] Herrmann, *Ber. Deutsch. Chem. Ges.* x. 646.
[10] Hanriot, *Compt. Rend.* cii. 1250.

The calculated quantity of pure phenol is dissolved in strong caustic soda solution, the whole evaporated to dryness and the residue rubbed into a dry powder; this is then gradually heated up to 180° in a metal retort in a current of carbon dioxide which has been previously warmed. After some time phenol commences to distil over, and is subsequently given off in larger quantity; the temperature is then raised to 200°, and the operation continued until no more phenol comes over. The residue is dissolved in water and fractionally precipitated with hydrochloric acid; resinous and colouring matters are first thrown down, followed by tolerably pure acid, which is re-crystallized from water and purified by distillation with superheated steam.[1]

According to another patented process, carbonyl chloride, which is now manufactured on a large scale, is passed into a mixture of sodium carbonate and phenate heated to 140°, the temperature being finally raised to 200°.[2]

Various hypotheses were proposed to explain the course of the reaction which occurs when sodium phenate is heated in a stream of carbon dioxide. The correct explanation was found by R. Schmitt.[3] Pure dry sodium phenate absorbs carbon dioxide with formation of *sodium phenylcarbonate*, $C_6H_5O.CO.ONa$, as a white powder which is instantly decomposed by water, phenol and sodium bicarbonate being formed. When heated in a closed tube to 120°—130°, it is converted quantitatively into monosodium salicylate. In Kolbe's reaction, this complete decomposition does not take place, and the monosodium salicylate reacts with the sodium phenate at a higher temperature, phenol being liberated:



$$NaO.C_6H_5 + CO_2 = \begin{array}{l} O.C_6H_5 \\ | \\ CO_2Na \end{array} = \begin{array}{l} C_6H_4.OH \\ | \\ CO_2Na. \end{array}$$

$$\begin{array}{l} C_6H_4.OH \\ | \\ CO_2Na \end{array} + NaO.C_6H_5 = \begin{array}{l} C_6H_4ONa \\ | \\ CO_2Na \end{array} + C_6H_5.OH.$$

Salicylic acid is, therefore, best prepared by bringing absolutely dry sodium phenate into an autoclave, pumping in rather more than the calculated quantity of carbon dioxide, the mass being kept cool during the absorption, or, better, adding it in the solid form, agitating for some time and then heating to 120°—130°.[1]

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[1] Rautert, *Compt. Rend.* viii. 537.

[2] *Ibid.* xviii. Ref. 90.

[3] *Journ. Prakt. Chem.* [2] xxxi. 397.

2172 Salicylic acid has a slightly acid, astringent and at the same time sweet taste; it dissolves slightly in cold, more readily in hot water, from which it crystallizes in fine needles, while it is deposited in monoclinic prisms from an alcoholic solution which is allowed to evaporate spontaneously.

100 parts of water dissolve at:

0°	15°	100°
0·085	0·225	7·925 parts.

Absolute alcohol and ether dissolve about half their weight of the acid;[2] it is also readily soluble in chloroform, differing in this respect from its isomerides, and is dissolved by solutions of the acetates and citrates of the alkali metals.[3]

Its aqueous solution is coloured deep violet by ferric chloride; free acids, especially acetic and hydrochloric acids, hinder the reaction.[4] It prevents the precipitation of copper salts by alkalis, while its isomerides have not this property.[5] Strong boiling nitric acid converts it into picric acid, and chromic acid oxidizes it to water, carbon dioxide and a little formic acid.[6]

It melts at 155°—156°,[7] and sublimes on gradual heating, but partially decomposes into carbon dioxide and phenol when rapidly heated. It is completely split up when heated to 250°—260° for two hours in a sealed tube; on cooling, the compound of these two substances, which has already been described, separates out (Part III. p. 102).[8] This decomposition also occurs when the acid is heated for a long time to 220°—230° with water, and more rapidly in presence of hydrochloric acid at 140°—150°.[9] Sodium amalgam only acts upon it in acid solution; a resinous substance, probably saliretin, being formed.[10] In order to test the purity of salicylic acid, a piece the size of a pea is ground up with five ccs. of concentrated sulphuric acid, in which it should form a perfectly colourless solution.[1] Its alcoholic solution evaporated on a watch-glass should yield perfectly clear and colourless crystals: if they are yellow or brown, the sample contains admixed resins or colouring matters, while if they are pink or violet, iron is present.

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[1] *Ber. Deutsch. Chem. Ges.* xvii. Ref. 624; Schmitt, *loc. cit.*

[2] On Solubility, &c., see Ost, *Journ. Prakt. Chem.* [2] xvii. 232; Bourgoin, *Bull. Soc. Chim.* xxix. 247; xxxi. 57.

[3] Rother, *Pharm. Journ. Trans.* 1886, 328.

[4] Pagliani, *Ber. Deutsch. Chem. Ges.* xii. 385.

[5] Weith, *ibid.* ix. 342.

[6] Kraut, *Ann. Chem. Pharm.* cl. 9.

[7] Hübner, *ibid.* clxii. 74.

[8] Klepl, *Journ. Prakt. Chem.* [2] xxv. 464.

[9] Gräbe, *ibid.* cxxxix. 143.

[10] Velden, *Journ. Prakt. Chem.* [2] xv. 164.

As salicylic acid decomposes so readily into carbon dioxide and phenol, Kolbe considered that it would, like the latter, be a powerful antiseptic, and subsequently verified this conclusion by experiment. It has very rapidly come into favour both for technical and household purposes, and is preferable to phenol because it has no smell and is not poisonous. Its isomerides, according to Kolbe, are not antiseptics.[2] Salicylic acid is also employed in medicine, both for external and internal application. Several physicians have observed that the acid prepared from winter-green oil acts more powerfully than that obtained artificially, but this may possibly be due to the fact that the acid which first came into the market contained a considerable amount of impurity.[3]

2173 *The Salicylates.* Salicylic acid was first thought to be a monobasic acid, but was afterwards regarded as dibasic. Piria observes on this point: "Salicylic acid differs in a most striking manner from other monobasic acids in forming acid ethers, which are more fitly compared with the acid ethers of polybasic acids than with the neutral ethers. In the course of researches which I have instituted upon this question, I have succeeded in finding the cause of this exception, or rather in showing that the behaviour of this acid is not exceptional. Salicylic acid, which has hitherto been looked upon as monobasic, is actually dibasic, and very markedly so; it forms salts with two equivalents of a base so readily that it is singular that they have remained so long unnoticed. In the following, I shall call salts containing one equivalent of base, which have been previously described, acid salicylates, and those discovered by me, containing two equivalents of base, neutral salicylates."[4]

This view was accepted by most chemists, but Kolbe considered it to be a monobasic hydroxy-acid. Further researches have shown that it is both a monobasic acid and a phenol, and therefore contains two hydrogen atoms which are easily replaced by metals. The salts thus obtained are usually called basic salicylates, while those formed by the replacement of the hydrogen of the carboxyl group are known as normal salicylates. The latter have recently been carefully examined by Milone.[1]

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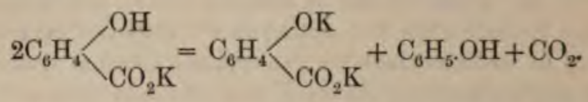
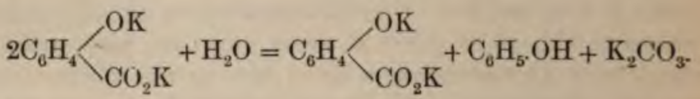
[1] Hager, *Fresenius' Zeitschr.* xvi. 259.
[2] *Journ. Prakt. Chem.* [2] xi. 9.
[3] Williams, *Yearbook of Pharm.* 1884, 424.
[4] *Ann. Chem. Pharm.* xciii. 262.

Potassium salicylate, $C_6H_4(OH)CO_2K$, is obtained by dissolving the acid in potassium carbonate solution, evaporating and extracting the residue with alcohol. It is deposited in needles on the spontaneous evaporation of its aqueous solution. When heated to 210°—220°, it decomposes quantitatively into basic potassium parahydroxybenzoate, phenol and carbon dioxide:



$$2C_6H_4\left<\begin{matrix}OH\\CO_2K\end{matrix}\right. = C_6H_4\left<\begin{matrix}OK\\CO_2K\end{matrix}\right. + C_6H_5.OH + CO_2.$$

If a solution of one molecule of the acid and two molecules of caustic potash be evaporated to dryness, and the residue heated to 220°, the basic salt of parahydroxybenzoic acid is also formed, together with phenol:



$$2C_6H_4\left<\begin{matrix}OK\\CO_2K\end{matrix}\right. + H_2O = C_6H_4\left<\begin{matrix}OK\\CO_2K\end{matrix}\right. + C_6H_5.OH + K_2CO_3.$$

If, however, three or more molecules of potash are employed, the salicylic acid is not changed; if four are taken, complete decomposition into carbon dioxide and phenol sets in at 300°, while in the presence of six molecules, the acid remains quite unaltered even at this temperature.[2] Rubidium salicylate behaves in a precisely similar manner on heating.[3]

Sodium salicylate, $C_6H_4(OH)CO_2Na$, forms silky tablets or a crystalline powder, and has an unpleasant sweet taste. It dissolves in its own weight of water and is used in medicine. On heating to above 200°, phenol and carbon dioxide are given off, the basic salt remaining behind, but not a trace of the para-acid is formed even at 300°. When salicylic acid is heated to this temperature with four molecules of caustic soda, it decomposes into phenol and carbon dioxide, while if eight molecules are added the greater portion of it remains unaltered (Ost).

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[1] *Gaz. Chim. Ital.* xv. 219.

[2] Ost, *Journ. Prakt. Chem.* [2] xi. 391.

[3] v. d. Velden, *ibid.* [2] xv. 151.

Inversely, sodium parahydroxybenzoate is converted into basic sodium salicylate, phenol and carbon dioxide, when it is heated to 290° in a current of carbon dioxide,[1] while hydroxyisophthalic acid, $C_6H_3(OH)(CO_2H)_2$, and hydroxytrimesic acid, $C_6H_2(OH)(CO_2H)_3$, are formed at temperatures above 300°.

When equal molecules of salicylic acid and its normal salt are dissolved in alcohol and the solution concentrated, hard, clear crystals of $C_7H_6O_3 + C_7H_5NaO_3$ are obtained, which are converted by water into pseudomorphs of salicylic acid.[2]

Lithium salicylate is converted into the basic salt at 300° without any formation of parahydroxybenzoic acid.

Thallium salicylate, $C_6H_4(OH)CO_2Tl$, is obtained by neutralizing the acid with thallium carbonate; its hot, concentrated solution deposits coarse needles on cooling. If the calculated quantity of thallium hydroxide be added to the solution, the basic salt, $C_6H_4(OTl)CO_2Tl$, separates out in yellow, nacreous, rhombic tablets, which are only very slightly soluble in water. This compound is also formed, together with phenol, when the normal salt is heated to 300°, while at a higher temperature the salicylic acid is partially converted into parahydroxybenzoic acid and hydroxyisophthalic acid (v. d. Velden).

Ammonium salicylate, $2C_6H_4(OH)CO_2NH_4 + H_2O$, forms readily soluble, monoclinic crystals; when heated in a current of ammonia it decomposes into phenol and ammonium carbonate. The methylamine and aniline salts behave in a similar manner, while tetra-ethylammonium salicylate decomposes on heating into tri-ethylamine and ethyl salicylate.[3]

Calcium salicylate, $(C_7H_5O_3)_2Ca + 2H_2O$, is readily soluble in water, and crystallizes in octohedra; when it is heated with a solution of calcium sucrate, or when salicylic acid is heated with an excess of milk of lime, the basic salt, $C_7H_4O_3Ca + H_2O$, is formed as a sandy, crystalline powder, which is almost insoluble in water and has an alkaline reaction (Piria).

Barium salicylate, $(C_7H_5O_3)_2Ba + H_2O$, is obtained by boiling the acid with water and barium carbonate; it crystallizes in stellate aggregates of silky needles. When baryta water is added to its boiling concentrated solution, the slightly soluble, alkaline, basic salt, $C_7H_4O_3Ba + 2H_2O$, separates out in small plates or needles.

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[1] Kupferberg, *Journ. Prakt. Chem.* [2] xiii. 104.
[2] Hofmann, *Arch. Pharm.* [3] xii. 226.
[3] Kupferberg, *Journ. Prakt. Chem.* [2] xvi. 437.

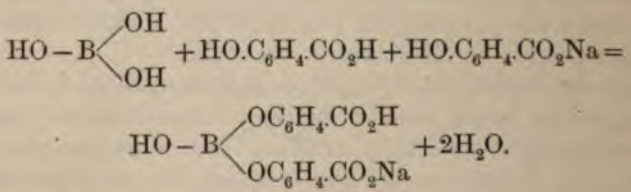
Lead salicylate, $(C_7H_5O_3)_2Pb + H_2O$, separates from boiling water in transparent crystals; when it is boiled with water, or when lead acetate is added to its hot solution, a slightly soluble, crystalline precipitate of $C_7H_4O_3Pb$ is formed. If, however, ammonia be added, and the solution boiled, the basic salt, $2(C_7H_4O_3)Pb + 3PbO$, is formed; it is a light powder consisting of micaceous plates.

Copper salicylate, $(C_7H_5O_3)_2Cu + 4H_2O$, is best prepared by decomposing the barium salt with copper sulphate; it crystallizes in long, bluish green needles, which are readily soluble in water, and on boiling with it form the basic salt, $C_7H_4O_3Cu + H_2O$, which is a yellowish green powder.

Basic copper potassium salicylate, $C_7H_4O_3Cu + C_7H_4O_3K_2 + 4H_2O$, is formed by adding salicylic acid to a solution of copper tartarate in tolerably strong caustic potash; a green mass of crystals is formed, which is dried on a porous plate and recrystallized from a little lukewarm water. Small, emerald-green, rhombic tablets are thus obtained, which are insoluble in alcohol, and form a dark blue solution in caustic potash. When the aqueous solution is boiled it becomes colourless and deposits black copper oxide. Barium chloride produces, on standing, a green, crystalline precipitate of $C_7H_4O_3Cu + C_7H_4O_3Ba + 4H_2O$.

Silver salicylate, $C_7H_5O_3Ag$, is a precipitate which crystallizes from boiling water in very lustrous, transparent needles.

Borondisalicylic acid, $B(OH)(OC_6H_4.CO_2H)_2$, is not known in the free state; its sodium salt is formed, along with free boric acid, when four molecules of salicylic acid are added to a boiling solution of one molecule of borax, as well as by dissolving a mixture of equal molecules of boric acid, salicylic acid and sodium salicylate:



$$HO-B\begin{cases}OH\\OH\end{cases} + HO.C_6H_4.CO_2H + HO.C_6H_4.CO_2Na =$$

$$HO-B\begin{cases}OC_6H_4.CO_2H\\OC_6H_4.CO_2Na\end{cases} + 2H_2O.$$

It forms crystalline crusts and is readily soluble in hot water and alcohol. Its aqueous solution turns turmeric paper brown, reddens litmus paper, and is coloured violet by ferric chloride; hydrochloric acid gives a precipitate of salicylic acid. Several other of its salts have been prepared; its barium salt is only slightly soluble in boiling water.[1]

2174 *Methyl salicylate*, $C_6H_4(OH)CO_2.CH_3$. Cahours, in 1843, found that winter-green oil, obtained from *Gaultheria procumbens* (Canadian tea), one of the Ericaceae, which occurs abundantly in the north of the United States and in Canada, consists of this compound together with small quantities of a terpene, and he prepared the ether by distilling salicylic acid with wood-spirit and sulphuric acid in order to compare the two products.[2] Since as a phenol it forms metallic salts, it was called gaultheriaïc acid and methylsalicylic acid, the latter name being now given to the following compound.

The ethereal oils of *Gaultheria punctata* and *Gaultheria leucocarpa*, which grow on the summits of extinct volcanoes in Java,[3] and of *Andromeda Lechenaultii*, one of the Ericaceæ, which occurs abundantly in the Neilgherry Mountains in India,[4] consist almost entirely of methyl salicylate.

It is a liquid with a pleasant, refreshing odour, and boils at 217°. Winter-green oil is largely used in America as a perfume; that obtained artificially, by heating salicylic acid with methyl alcohol and sulphuric acid, does not possess the fine odour of the natural product.

Methylsalicylic acid, $C_6H_4(OCH_3)CO_2H$. Cahours obtained the methyl ether of this compound by the action of methyl iodide and caustic potash on winter-green oil. It is a liquid boiling at 244°—246° (Schreiner). In order to prepare the acid, two parts of methyl salicylate are heated to 100°—120° with one part of caustic potash and three or four parts of methyl iodide, the product distilled in order to remove methyl alcohol and methyl iodide, and the residue then extracted with caustic soda and precipitated with hydrochloric acid. Any adhering salicylic acid is removed by boiling with an excess of milk of lime, insoluble basic calcium salicylate being precipitated, while calcium methylsalicylate remains in solution, and is then decomposed by hydrochloric acid.[5]

Methylsalicylic acid crystallizes from hot water in large, monoclinic tablets, and from alcohol in prisms, which melt at 98·5° and decompose above 200° into carbon dioxide and anisol.

[1] Jahns, *Arch. Pharm.* [3] xii. 212.

[2] *Ann. Chem. Pharm.* xlviii. 83; liii. 327.

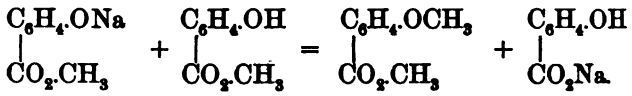
[3] de Vrij, *Pharm. Journ. Trans.* [3] ii. 503; Köhler, *Ber. Deutsch. Chem. Ges.* xii. 246.

[4] Broughton, *Pharm. Journ. Trans.* [3] ii. 281.

[5] Gräbe, *Ann. Chem. Pharm.* cxxxix. 137.

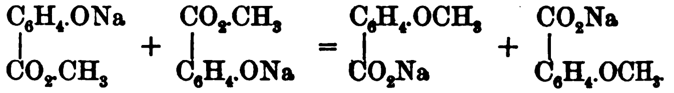
On heating with concentrated hydrochloric acid, it is resolved into salicylic acid and methyl chloride; hydriodic acid has a similar action.

The sodium salt of the acid is formed, together with a little of the methyl ether and sodium salicylate, when winter-green oil is heated with sodium:



$$\begin{array}{l}C_6H_4.ONa\\ |\\ CO_2.CH_3\end{array} + \begin{array}{l}C_6H_4.OH\\ |\\ CO_2.CH_3\end{array} = \begin{array}{l}C_6H_4.OCH_3\\ |\\ CO_2.CH_3\end{array} + \begin{array}{l}C_6H_4.OH\\ |\\ CO_2Na.\end{array}$$

Two molecules of the sodium compound then react in a similar manner:



$$\begin{array}{l}C_6H_4.ONa\\ |\\ CO_2.CH_3\end{array} + \begin{array}{l}CO_2.CH_3\\ |\\ C_6H_4.ONa\end{array} = \begin{array}{l}C_6H_4.OCH_3\\ |\\ CO_2Na\end{array} + \begin{array}{l}CO_2Na\\ |\\ C_6H_4.OCH_3.\end{array}$$

ETHEREAL SALTS OF SALICYLIC ACID.

		Melting point.	Boiling point.
[2] Ethyl salicylate, $C_6H_4(OH)CO_2.C_2H_5$,	liquid	—	223°
[3] Propyl salicylate, $C_6H_4(OH)CO_2.C_3H_7$,	liquid	—	239°
[4] Amyl salicylate, $C_6H_4(OH)CO_2.C_5H_{11}$,	liquid	—	270°
[5] Ethylene salicylate, $(C_6H_4(OH)CO_2)_2C_2H_4$,	needles	83°	—
[6] Propenyl salicylate, $C_6H_4(OH)CO_2C_3H_5(OH)_2$,	liquid	—	—

SALICYLIC ETHERS.

	Melting-point.
[7] Ethysalicylic acid, $C_6H_4(OC_2H_5)CO_2H$, gradually solidifying oil	19·4°
[8] Isopropylsalicylic acid, $C_6H_4(OC_3H_7)CO_2H$, liquid .	—
[9] Benzylsalicylic acid, $C_6H_4(OC_7H_7)CO_2H$, small tablets	75°
[10] Ethylenesalicylic acid, $C_6H_4(OC_6H_4.CO_2H)_2$, long needles	151°–152°

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[1] *Ann. Chem. Pharm.* cxlii. 327.

[2] Baly, *ibid.* lxx. 269; Schreiner, *ibid.* cxcvii. 17; Gottig, *Ber. Deutsch. Chem. Ges.* ix. 1473.

[3] Cahours, *Jahresb. Chem.* 1874, 333.

[4] Drion, *Ann. Chem. Pharm.* xcii. 313.

[5] Gilmer, *ibid.* cxxvii. 377.

[6] Göttig, *Ber. Deutsch. Chem. Ges.* x. 1817.

[7] Kraut, *Ann. Chem. Pharm.* cl. 1; Göttig, *Ber. Deutsch. Chem. Ges.* ix. 1474.

[8] Kraut.

[9] Perkin, *Journ. Chem. Soc.* xxi. 125.

[10] Weddige, *Journ. Prakt. Chem.* [2] xxi. 128.

ETHEREAL SALTS OF SALICYLIC ETHERS.

	Boiling-point.
[1] Ethyl methylsalicylate, $C_6H_4(OCH_3)CO_2.C_2H_5$,	260°
[2] Methyl ethylsalicylate, $C_6H_4(OC_2H_5)CO_2.CH_3$,	256°—257°
[3] Ethyl ethylsalicylate, $C_6H_4(OC_2H_5)CO_2.C_2H_5$,	258°—259°
[4] Methyl isopropylsalicylate, $C_6H_4(OC_3H_7)CO_2.CH_3$,	250°
[5] Methyl benzylsalicylate, $C_6H_4(OC_7H_7)CO_2.CH_3$,	above 320°

	Melting-point.
[6] Ethyl ethylenesalicylate, $C_2H_4(OC_6H_4.CO_2C_2H_5)_2$, thick plates	96°—97°

Phenyl salicylate, $C_6H_4(OH)CO_2.C_6H_5$. Seifert[7] obtained this compound by heating salicylic acid and phenol with phosphorus oxychloride:

$$2C_6H_4(OH)CO_2H + 2C_6H_5.OH + POCl_3 = 2C_6H_4(OH)CO_2.C_6H_5 + 3HCl + HPO_3.$$

A better yield is obtained by employing the sodium salts; this ethereal salt, known as *salol*, is manufactured by heating the product of the action of carbon dioxide on sodium phenate with phosphorus pentachloride or oxychloride:

$$C_6H_4(OH)CO_2Na + C_6H_5.ONa + PCl_5 = C_6H_4(OH)CO_2.C_6H_5 + 2NaCl + POCl_3.$$

$$2C_6H_4(OH)CO_2Na + 2C_6H_5.ONa + POCl_3 = 2C_6H_4(OH)CO_2.C_6H_5 + 3NaCl + NaPO_3.$$

Salol crystallizes in rhombic prisms, which are odourless and melt at 42°—42·5°; the dilute alcoholic solution, however, has a smell resembling that of winter-green oil. It is employed in medicine as a substitute for salicylic acid, because, as it is not decomposed until it reaches the duodenum, it does not attack the stomach like the former: when applied externally it has no corrosive action, and, on account of its lower melting-point, it can be more conveniently used for dressings, &c., than salicylic acid.

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[1] Gräbe; Schreiner; *loc. cit.*

[2] Schreiner; *loc. cit.*

[3] Göttig; Schreiner; *loc. cit.*

[4] Kraut; *loc. cit.*

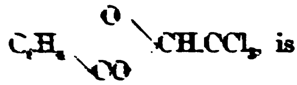
[5] Perkin; *loc. cit.*

[6] Weddige; *loc. cit.*

[7] *Journ. Prakt. Chem.* [2] xxxi. 462.

Phenyl methylsalicylate, $C_6H_4(OCH_3)CO_2C_6H_5$, was prepared by Seifert in a similar manner; it crystallizes in six-sided prisms, melting at 59°.

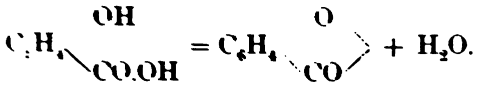
Acetylsalicylic acid, $C_6H_4(O.CO.CH_3)CO_2H$, is formed by the action of acetyl chloride on salicylic acid or its sodium salt, and crystallizes from hot water in fine needles, melting at 118°—118·5°. Its aqueous solution gives a violet colouration with ferric chloride; when the acid is heated with ammonia, ammonium salicylate is formed, but no salicylamide (Kraut).

Salicyl-chloralide, 
$C_6H_4\left\langle\begin{matrix}O\\CO\end{matrix}\right\rangle CH.CCl_3$, is formed when salicylic acid is heated to 130°—150° for a long time with an excess of chloral. It is insoluble in water, slightly soluble in alcohol and ether and crystallizes from the latter in prisms, melting at 124°—125°.[1]

Disalicylic acid, $(C_6H_4.CO_2H)_2O$. This compound, which is also called salicylic anhydride, or salicylosalicylic acid, was obtained by Gerhardt by the action of phosphorus oxychloride on sodium salicylate.[2]

It is also formed when acetylsalicylic acid is heated, or when salicylic acid is heated for a long time to 130°—140° with acetyl chloride.[3] It is an amorphous mass, which dissolves in the alkaline carbonates and is reprecipitated by acids. It gives no colouration with ferric chloride; aqueous ammonia converts it into salicylamide and ammonium salicylate, while potassium salicylate is formed by the action of caustic potash.

Salicylide, $C_7H_4O_2$, is formed by heating salicylic acid with phosphorus oxychloride:


$$C_6H_4\left\langle\begin{matrix}OH\\CO.OH\end{matrix}\right. = C_6H_4\left\langle\begin{matrix}O\\CO\end{matrix}\right\rangle + H_2O.$$

It crystallizes from absolute alcohol in spherical aggregates of lustrous plates, which melt at 195°—200°; it gives no colouration with ferric chloride, and is converted into salicylic acid by the action of caustic potash.[4]

Tetrasalicylide, $C_{28}H_{18}O_9$, is formed at the same time as the preceding compound, and is a resinous mass insoluble in alcohol.

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[1] Wallach, *Ann. Chem. Pharm.* cxcvii. 41.

[2] *Ibid.* lxxxvii. 159.

[3] Kraut, *ibid.* cl. 13.

[4] Schiff, *ibid.* clxiii. 220.

Salicylhydroxyacetic acid, $C_6H_4(OCH_2CO_2H)CO_2H$, is obtained by oxidizing ortho-aldehydophenoxyacetic acid (p. 289) with potassium permanganate. It crystallizes from hot water in white needles, melting at 186°—187°. It forms readily soluble salts which crystallize well.[1]

2175 *The Action of Phosphorus Pentachloride upon Salicylic Acid.* As already mentioned, Chiozza found, in 1852, that when salicylic acid is treated with phosphorus pentachloride and the product distilled, the distillate yields orthochlorobenzoic acid when treated with water (p. 217). Gerhardt repeated this experiment, and found that the liquid before distillation is salicyl chloride, $C_7H_5O_2Cl$, as it is converted by water into salicylic acid, and by alcohol into an ethereal salt of this; he also obtained it together with methyl alcohol by treating winter-green oil with phosphorus pentachloride.[2] Drion made the further observations that only a trace of phosphorus oxychloride is formed in this reaction, and that a portion of the product is converted into chlorobenzoyl chloride by distillation.[3]

Couper, however, obtained different results. He acted upon one molecule of methyl salicylate with two molecules of phosphorus chloride, and distilled the resulting liquid; the excess of the chloride came over first, followed by a liquid distilling between 285°—295°, to which he gave the name of salicyl trichlorophosphate, explaining its formation by the following equation:

$$C_8H_8O_3 + PCl_5 = HCl + CH_3Cl + C_7H_4Cl_3PO_3.$$

This compound, which he also obtained from salicylic acid, is decomposed by water into hydrochloric acid, phosphoric acid and salicylic acid:

$$C_7H_4Cl_3PO_3 + 4H_2O = 3HCl + H_3PO_4 + C_7H_6O_3.$$

When he submitted it to rapid distillation, a considerable quantity of hydrochloric acid was evolved, and the distillate consisted of a liquid boiling above 300°, which deposited large crystals of *salicyl monochlorophosphate*, $C_7H_4ClPO_4$, when preserved in a sealed tube; this substance, like the trichlorophosphate, is converted into *phosphosalicylic acid*, $C_7H_7PO_6$, in moist air. He therefore considered that the existence of salicyl

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[1] Rössing, *Ber. Deutsch. Chem. Ges.* xvii. 2988.

[2] *Ann. Chem. Pharm.* lxxxix. 363.

[3] *Ibid.* xcii. 312.

[illegible] an analysis of which has been published, was very [illegible]

[illegible] that although the latter compound had not been obtained in a state of purity its existence was proved [illegible] salicylic acid are formed by the action of [illegible]

[illegible] came to the same conclusion. According [illegible] chloride, salicyl chloride and [illegible] is obtained by distilling salicylic acid with phosphorus pentachloride. Kekulé, who investigated this reaction at about the same period, found that when the product is heated to [illegible] to remove phosphorus chloride [illegible] remained which yielded salicylic acid and [illegible] when decomposed by water. It also [illegible] considerably more chlorine [illegible] salicyl chloride, on distillation [illegible] considerable quantities of phosphorus [illegible] chloride, but not Couper's compound.

[illegible] the generally accepted view, that the [illegible] compounds are formed by the action of phosphorus [illegible] salicylic acid:

[illegible]	[illegible]	Chlorosalicyl chloride.	Chlorobenzenyl trichloride.
	[illegible]	[illegible]	Cl
[illegible]		[illegible]	C_6H_4
	[illegible]	COCl	CCl_3

[illegible] could not be obtained pure because it [illegible] distillation, and could not therefore be fre[illegible] chloride and phosphorus oxychloride [illegible] adheres most obstinately to th[illegible]

[illegible] product was found by Anschütz, who, b[illegible] molecules of salicylic acid and phos[illegible] obtained an evolution of hydrochloric aci[illegible] liquid which distilled under a pressure of 11 mm [illegible] only a small quantity of residu[illegible]. This has the composition of Couper's salicyl tri-

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[1] Ann. Chem. Pharm. cix. 369.

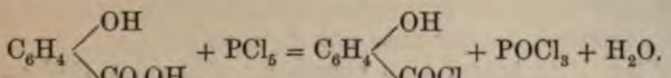
[2] [illegible] 188.

[illegible] Chem. Phys. [3] [illegible]

[3] Ibid. cix. 373.

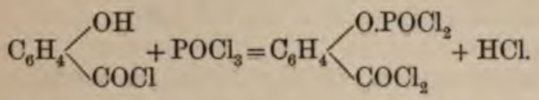
[4] Ibid. cxvii. 148.

chlorophosphate and is orthocarbonylphenylphosphoryl chloride, formed according to the following equations:



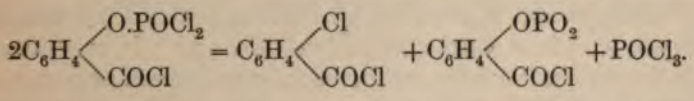
$$C_6H_4\left\langle\begin{matrix}OH\\CO.OH\end{matrix}\right. + PCl_5 = C_6H_4\left\langle\begin{matrix}OH\\COCl\end{matrix}\right. + POCl_3 + H_2O.$$

The phosphorus oxychloride then acts upon the salicyl chloride just as it does upon phenol:



$$C_6H_4\left\langle\begin{matrix}OH\\COCl\end{matrix}\right. + POCl_3 = C_6H_4\left\langle\begin{matrix}O.POCl_2\\COCl_2\end{matrix}\right. + HCl.$$

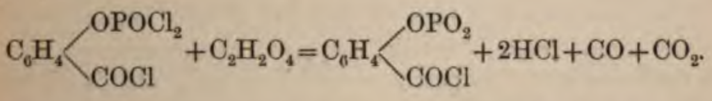
The pure chloride distils at 285°—295° under the ordinary pressure. If it be submitted to slow distillation, a mixture of phosphorus oxychloride, orthochlorobenzoyl chloride and orthochlorotribenzenyl chloride is obtained, boiling at 270°—290°. If the distillation be now continued under diminished pressure, Couper's salicyl monochlorophosphate, or *orthochlorocarbonylphenyl metaphosphate* passes over; it is formed, together with orthochlorobenzoyl chloride, according to the following equation:



$$2C_6H_4\left\langle\begin{matrix}O.POCl_2\\COCl\end{matrix}\right. = C_6H_4\left\langle\begin{matrix}Cl\\COCl\end{matrix}\right. + C_6H_4\left\langle\begin{matrix}OPO_2\\COCl\end{matrix}\right. + POCl_3.$$

It boils at 187° under a pressure of 11 mm., and solidifies on cooling to crystals, which melt at 30°.

The chloride is decomposed by a small quantity of water into hydrochloric acid, phosphoric acid and salicylic acid; in moist air, on the other hand, or on distillation with anhydrous oxalic acid, it is converted into orthochlorocarbonylphenyl metaphosphate:



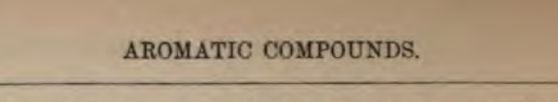
$$C_6H_4\left\langle\begin{matrix}OPOCl_2\\COCl\end{matrix}\right. + C_2H_2O_4 = C_6H_4\left\langle\begin{matrix}OPO_2\\COCl\end{matrix}\right. + 2HCl + CO + CO_2.$$

It dissolves, however, in a large quantity of cold water, with formation of *orthocarboxylphenylphosphoric acid*, $C_6H_4(CO.OH)OPO(OH)_2$, which on evaporation in a vacuum over soda lime gives a crystalline mass, which melts at 147° and is readily soluble in water.

If the chloride be heated to 165°—170° with phosphorus pentachloride, *benzenyltrichlorophosphoryl chloride*, $C_6H_4(OPOCl_2)$

CCl_3, is formed; it is a powerfully refractive liquid, which boils at 178°—179° under a pressure of 11—12 mm., and is not converted by water into hydroxybenzenyl trichloride, as might have been expected, but into phosphosalicylic acid.

When it is heated with phosphorus chloride to 180°, orthochlorobenzenyl trichloride is formed:[1]



$$C_6H_4\begin{cases}OPOCl_2\\CCl_3\end{cases} + PCl_5 = C_6H_4\begin{cases}Cl\\CCl_3\end{cases} + 2POCl_3.$$

2176 *Salicylamide*, $C_6H_4(OH)CO.NH_2$, is obtained by the action of concentrated ammonia on methyl salicylate;[2] it crystallizes from ether in lustrous, yellow plates, melting at 142°,[3] and sublimes when carefully heated. As a phenol it forms metallic salts; its ethers are formed when ammonia is allowed to act upon the ethers of salicylic acid.

Benzoylsalicylamide, $C_6H_5(O.CO.C_6H_5)NH_2$, is formed when salicylamide is heated to 180° with benzoyl chloride, or fused with benzamide.[4] It is slightly soluble in alcohol, but almost insoluble in ether, and crystallizes in needles melting at 200°.

Disalicylamide, $(C_6H_4(OH)CO)_2NH$, is prepared by heating salicylic acid in a current of hydrochloric acid. It crystallizes in yellowish white needles, which resemble asbestos in appearance, and melt at 197°—199° with partial decomposition; it is insoluble in water, but readily dissolves in alcohol and alkalis. The alcoholic solution is coloured red by ferric chloride.[5]

Salicylanilide, $C_6H_4(OH)CO.NH(C_6H_5)$, is obtained by gently warming aniline with salicylic acid and then gradually adding phosphorus trichloride to the cooled mass. It crystallizes from dilute alcohol in small prisms, melting at 134°—135°; ferric chloride colours the solution violet.[6]

Salicyluric acid, $C_6H_4(OH)CO.NH.CH_2.CO_2H$. When salicylic acid is administered internally, it appears in the urine partly in an unaltered state and partly as salicyluric acid. This is slightly soluble in water, readily in alcohol, and crystallizes in fine needles, which melt at 160° and give a violet colouration with ferric chloride. On heating with concentrated hydrochloric acid, it decomposes into salicylic acid and amido-acetic acid. Its barium salt forms prisms, which are only slightly soluble in water.[1]

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[1] Anschütz, *Ann. Chem. Pharm.* ccxxviii. 308, and private communication.
[2] Limpricht, *ibid.* xcviii. 258.
[3] Grimaux, *Bull. Soc. Chim.* xiii. 25.
[4] Chiozza and Gerhardt, *Jahresb. Chem.* 1856, 502.
[5] Schulerud, *Journ. Prakt. Chem.* [2] xxii. 298.
[6] Kupferberg, *ibid.* [2] xvi. 442; Wanstrat, *Ber. Deutsch. Chem. Ges.* vi. 336.

Salicylnitril, $C_6H_4(OH)CN$, is formed by heating the amide with phosphorus pentoxide, and is a colourless, crystalline substance, which melts at 195°, and on boiling with dilute caustic potash is converted into salicylic acid.[2]

Polysalicylnitril, $(C_7H_5ON)_x$. Limpricht obtained this compound by heating salicylamide to 270°, and looked upon it as an imide of the dibasic salicylic acid.[3] It is a yellow, crystalline powder, which melts at 280°—285° (Grimaux), and is only converted into salicylic acid by fusion with caustic potash. On heating with phosphorus pentachloride, orthochlorobenzonitril is formed.[4]

Benzoylsalicylnitril, $C_6H_4(OCO.C_6H_5)CN$, was prepared by Limpricht by heating benzosalicylamide, and called by him benzoylsalicylimide.[5] Henry obtained it by heating the polynitril with benzoyl chloride. It crystallizes from hot alcohol in small, brittle, lustrous plates, melting at 148°—149°. The hot alcoholic solution is coloured red by ferric chloride.

SUBSTITUTION PRODUCTS OF SALICYLIC ACID.

2177 *Chlorosalicylic acid*, $C_6H_3Cl(OH)CO_2H\,(5:2:1)$, is formed by passing chlorine into a solution of salicylic acid in carbon disulphide,[6] as well as by the action of nitrous acid upon β-chloramidobenzoic acid.[7] It may also be obtained by replacing the amido-group of the corresponding amidosalicylic acid by chlorine,[8] and by heating parachlorophenol with tetrachloromethane and alcoholic potash.[9] It dissolves in 1100 parts of water at 20°, and in 80 parts at 100°, and crystallizes in small needles, melting at 172°. The aqueous solution is coloured violet by ferric chloride.

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[1] Bertagnini, *Ann. Chem. Pharm.* xcvii. 249.

[2] Grimaux, *Bull. Soc. Chim.* xiii. 26.

[3] *Ann. Chem. Pharm.* xcviii. 261.

[4] Henry, *Ber. Deutsch. Chem. Ges.* ii. 491.

[5] *Ann. Chem. Pharm.* xcix. 250.

[6] Hübner and Brenken, *Ber. Deutsch. Chem. Ges.* vi. 174.

[7] Hübner and Weiss, *ibid.* vi. 175.

[8] Schmitt, *Jahresb. Chem.* 1864, 385; Beilstein, *Ber. Deutsch. Chem. Ges.* viii. 816.

[9] Hasse, *ibid.* x. 2190.

Dichlorosalicylic acid, $C_6H_2Cl_2(OH)CO_2H(3:5:2:1)$, may be prepared by heating salicylic acid with antimony pentachloride,[1] as well as by the action of chlorine on a solution of salicylic acid in glacial acetic acid.[2] It is also slightly soluble in boiling water, and crystallizes from dilute alcohol in small prisms, which melt at 214°, and are coloured dark violet by ferric chloride. Concentrated nitric acid converts it into the same dichloronitrophenol as is formed by the nitration of α-dichlorophenol.[3]

α-Bromosalicylic acid, $C_6H_3Br(OH)CO_2H(3:2.1)$, has been obtained from the corresponding amidobromobenzoic acid.[4] It crystallizes in small, soluble needles, melting at 219°—220°, and gives a dark reddish blue colouration with ferric chloride.

β-Bromosalicylic acid $(5:2:1)$ is formed by the direct bromination of salicylic acid,[5] and also by treating β-bromamidobenzoic acid with nitrous acid (Hübner and Heinzerling). It crystallizes from hot water in long needles, melting at 164°—165°; ferric chloride colours it violet.

Three dibromosalicylic acids are also known.[6]

Iodosalicylic acid, $C_6H_3I(OH)CO_2H(5:2:1)$, has been prepared from the corresponding amido-salicylic acid by means of the diazo-reaction.[7] It is almost insoluble in cold water, and crystallizes from alcohol in needles, which melt at 196°, and decompose into iodophenol and carbon dioxide when they are rapidly heated. The same acid had previously been obtained by Lautemann by treating salicylic acid with iodine and caustic potash solution,[8] while Liechti[9] and Demole,[10] by the action of iodine and iodic acid on salicylic acid, prepared an iodosalicylic acid which is slightly soluble in cold, somewhat more readily in hot water, and crystallizes in needles, melting at 183°.

Two isomeric acids are therefore produced by the direct action of iodine on salicylic acid,[11] and probably in varying proportions. The following compounds are also formed in this reaction:

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[1] Lössner, *Journ. Prakt. Chem.* [2] xiii. 429.

[2] Smith, *Ber. Deutsch. Chem. Ges.* xi. 1225.

[3] Smith and Knerr, *Amer. Chem. Journ.* viii. 95.

[4] Hübuer and Heinzerling, *Zeitschr. Chem.* 1871, 709.

[5] Henry, *Ber. Deutsch. Chem. Ges.* ii. 275; Hübner and Heinzerling.

[6] Rollwage, *ibid.* x. 1707; Smith, *ibid.* 1706; Hübner, *ibid.* 1706.

[7] Goldberg, *Journ. Prakt. Chem.* [2] xix. 368; Hübner, *Ber. Deutsch. Chem. Ges.* xii. 1347.

[8] *Ann. Chem. Pharm.* cxx. 302.

[9] *Ibid.* Suppl. vii. 136.

[10] *Ber. Deutsch. Chem. Ges.* vii. 1437.

[11] Fischer, *Ann. Chem. Pharm.* clxxx. 346.

Di-iodosalicylic acid, $C_6H_2I_2(OH)CO_2H$, is best obtained by the action of iodine and mercuric oxide upon an alcoholic solution of salicylic acid.[1] It is slightly soluble in cold, more readily in hot water and alcohol, crystallizes in needles, melting at 220°—230°, and, like moniodosalicylic acid, is coloured violet by ferric chloride.

Tri-iodosalicylic acid, $C_6HI_3(OH)CO_2H$, is insoluble in water, and crystallizes from alcohol in yellow needles.

2178 *Nitrosalicylic acids.* In the year 1806, Fourcroy and Vauquelin obtained a volatile, crystalline acid, which they thought was benzoic acid, by treating indigo blue with dilute nitric acid. Chevreul recognized the individuality of this substance, which was called indigotic acid, and it was then carefully examined by Buff,[2] and correctly analysed by Dumas.[3] Marchand[4] confirmed the results obtained by Dumas, and found, as also did Gerhardt,[5] that indigotic acid is identical with nitrosalicylic acid. Piria, by the action of nitric acid on salicin, obtained helicin and anilotic acid, which, according to Major, is identical with nitrosalicylic acid, although Piria himself was convinced that the two acids were different substances.[6] In spite of this, it was generally assumed that only one nitrosalicylic acid existed, until Hübner found that two are formed by the nitration of salicylic acid.[7] One of these is identical with anilotic acid, while indigotic acid proves to be a mixture of both.[8] These acids are also formed when the vapour of nitric acid is passed into methyl salicylate.[9]

a-Nitrosalicylic acid, $(CO_2H:OH:NO_2 = 1:2:5)$, may be obtained, in addition to the methods given above, by heating paranitrophenol with tetrachloromethane and alcoholic potash to 100°,[10] by boiling ε-nitro-amidobenzoic acid with caustic potash solution,[11] and by passing nitrogen tetroxide into a cold aqueous solution of salicylic acid (Hübner). In order to prepare it, 100 parts of salicylic acid are dissolved in 800 parts of glacial acetic acid, 50 parts of pure nitric acid, of sp. gr. of 1·5, being then gradually added to the cold; the solution is then diluted with two or three volumes of water, and the acid, which separates out after some time, purified by repeated crystallization from hot water. The barium salt of the β-acid may be prepared from the mother-liquor; it is only slightly soluble in water.

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[1] Weselsky, *Ann. Chem. Pharm.* clxxiv. 103.
[2] Schweigg, *Journ. Chem. Phys.* li. 38; liv. 163.
[3] *Ann. Chim. Phys.* [3] ii. 224.
[4] *Journ. Prakt. Chem.* xxvi. 385.
[5] *Ann. Chem. Pharm.* xlv. 19.
[6] *Ibid.* xcvii. 253.
[7] *Ibid.* cxcv. 1.
[8] Masino and Schiff, *ibid.* cxcviii. 256.
[9] Smith and Knerr; *Amer. Chem. Journ.* viii. 99.
[10] Hasse, *Ber. Deutsch. Chem. Ges.* x. 2188.
[11] Griess, *ibid.* xi. 1730.

α-Nitrosalicylic acid crystallizes in long needles, which melt at 228° and dissolve in 1475 parts of water at 15°; it is more easily soluble in alcohol or hot water. Its solution is coloured blood-red by ferric chloride. Boiling nitric acid converts it into picric acid, and when its diethyl ether is heated to 130° with alcoholic ammonia, the amide of ε-amidonitrobenzoic acid is obtained. On heating with lime it decomposes into carbon dioxide and paranitrophenol.

Normal barium α-nitrosalicylate, $(C_7H_4NO_5)_2Ba + 4H_2O$,[1] is obtained by heating the acid with water and barium carbonate; it is readily soluble in water, and crystallizes in compact, yellow needles which form fascicular aggregates. The basic salt, $C_7H_3NO_5Ba + 2H_2O$, is formed by boiling the acid with baryta water, and crystallizes in citron-yellow plates, which have a satin lustre and are only slightly soluble in water.

β-Nitrosalicylic acid, or *Anilic acid*, ($CO_2H : OH : NO_2 = 1 : 2 : 3$), is formed in largest quantity by the action of the most concentrated nitric acid upon salicylic acid at a low temperature,[2] and has also been obtained by heating orthonitrophenol with tetrachloromethane and alcoholic potash (Hasse). In order to prepare it, 10 grms. of salicylic acid are gradually brought into a mixture of 10 grms. of concentrated nitric acid with 10—12 grms. of glacial acetic acid at a temperature of about 6°. The solution is then poured into 250 ccm. of water and the precipitated acids separated by means of their barium salts.

β-Nitrosalicylic acid dissolves in 770 parts of water at 15·5°, readily in alcohol and ether, and crystallizes in long needles, which contain a molecule of water, and melt at 125°. The anhydrous acid melts at 144°; its solution is coloured blood-red by ferric chloride; on heating with lime it decomposes into carbon dioxide and orthonitrophenol, while the amide of ζ-amidonitrobenzoic acid is formed by the action of alcoholic ammonia on its diethyl ether.

Normal barium β-nitrosalicylate, $(C_7H_4NO_5)_2Ba$, crystallizes in golden yellow plates or compact, refractive needles, which are only very slightly soluble in cold, more readily in hot water. Ammonia added to the solution produces a deep-red colouration and then a precipitate of the basic salt, $2C_7H_3NO_5Ba + 3H_2O$, in thick, blood-red needles.

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[1] *Ann. Chem. Pharm.* ccx. 344.

[2] Schaumann, *Ber. Deutsch. Chem. Ges.* xii. 1346.

Dinitrosalicylic acid, $C_6H_2(NO_2)_2(OH)CO_2H$. The methyl ether of this compound was obtained by Cahours by dropping winter-green oil into a mixture of fuming nitric and sulphuric acids.[1] It crystallizes in yellow scales, which melt at 127°—128° (Salkowski), and are easily saponified by caustic potash. Stenhouse then prepared dinitrosalicylic acid by the action of nitric acid on the aqueous extracts of *Populus nigra* and *P. balsamifera*, which contain populin.[2] It is also formed by the further nitration of both the mononitrosalicylic acids, their constitution being thus shown. It is best prepared by bringing 10 grms. of salicylic acid into 70 grms. of the most concentrated nitric acid at 0°, and pouring the clear solution into 300 ccm. of water; after standing for 24—36 hours the separated acid is filtered off, pressed, converted into the barium salt by boiling with water and barium carbonate, and re-precipitated by hydrochloric acid.[3]

Dinitrosalicylic acid is readily soluble in cold, very readily in hot water, and crystallizes therefrom in thick, lustrous plates, or, on rapid cooling, in fine needles containing one molecule of water. Its solution is coloured dark-red by ferric chloride; on heating with water to 200° it decomposes into carbon dioxide and ordinary dinitrophenol.

Potassium-dinitrosalicylate. When caustic potash is added in excess to the aqueous solution of the acid, the salt $C_6H_2(NO_2)_2(OK)CO_2K + H_2O$ is formed; it crystallizes in long, dark-red needles, which detonate violently when heated. Dilute hydrochloric acid or nitric acid added to its solution precipitates the salt $C_6H_2(NO_2)_2(OH)CO_2K$, which crystallizes from boiling water in compact, short, dark yellow needles.

Barium dinitrosalicylate, $C_6H_2(NO_2)_2OBaCO_2 + 3H_2O$, forms compact, yellow needles, which are only slightly soluble in cold water.

2179 *a-Amidosalicylic acid*, $C_6H_3(NH_2)(OH)CO_2H$, was obtained by Beilstein by reducing nitrosalicylic acid with tin and hydrochloric acid;[4] it is better, however, to employ acetic acid (Hübner). It crystallizes in needles which have a satin lustre, and are insoluble in alcohol and cold water, but slightly soluble in hot water; the solution soon decomposes in the air, a brown, amorphous substance being precipitated. Ferric chloride produces a cherry-red colouration, followed by a brownish black precipitate.

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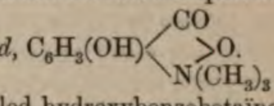
[1] *Ann. Chem. Pharm.* lxix. 232.

[2] *Ibid.* lxxviii. 1.

[3] Hübner, *ibid.* cxcv. 45.

[4] *Ann. Chem. Pharm.* cxxx. 243.

Amidosalicylic acid forms salts both with bases and acids; it decomposes on heating into carbon dioxide and paramidophenol.[1]



Trimethylamidosalicylic acid, $C_6H_3(OH){<}\begin{array}{l}CO\\N(CH_3)_3\end{array}{>}O$. This compound, which may also be called hydroxybenzobetaïne, is formed by the action of methyl iodide and caustic potash on amidosalicylic acid, and crystallizes from water in large, snow-white needles, often an inch in length, which contain four molecules of water, have a very bitter taste and are coloured reddish violet by ferric chloride. It combines with the mineral acids to form salts which crystallize well.

Methyl dimethylamidosalicylate, $C_6H_3(OH)N(CH_3)_2CO_2CH_3$, is prepared by heating the preceding compound, after previously removing its water of crystallization. It forms rhombic prisms, and is decomposed on boiling with hydrochloric acid into methyl alcohol and dimethylamidosalicylic acid, which crystallizes in small, almost insoluble needles.[2]

β-Amidosalicylic acid is not known in the free state; its hydrochloride crystallizes in needles which readily decompose (Hübner).

Nitro-amidosalicylic acid, $C_6H_2(NO_2)NH_2(OH)CO_2H$, is formed by the partial reduction of dinitrosalicylic acid; it forms crystals, melting at 220°; *a*-nitrosalicylic is obtained[3] when the amido-group is replaced by hydrogen.

Diamidosalicylic acid, $C_6H_2(NH_2)(OH)CO_2H$, was prepared by Saytzew by the action of hydriodic acid on the methyl ether of dinitrosalicylic acid.[4] It is very slightly soluble in cold, more readily in hot water, and crystallizes in small needles. It combines with acids to form salts which crystallize well; ferric chloride produces a brownish red colouration, followed by a black precipitate.

Sulphosalicylic acid, $C_6H_3(SO_3H)(OH)CO_2H$, was obtained by Mendius by the action of sulphur trioxide on salicylic acid,[5] and may also be prepared by heating salicylic acid with sulphuric acid.[1] It crystallizes in long, thin, very soluble needles, which melt at 120°, and are coloured an intense reddish violet by ferric chloride. Its salts crystallize well; on fusion with caustic potash, no dihydroxybenzene is formed, the product consisting entirely of phenol and salicylic acid.

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[1] Schmitt, *Jahresber.* 1864, 423.

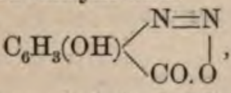
[2] Griess, *Ber. Deutsch. Chem. Ges.* xii. 2307.

[3] Babcock, *ibid.* xii. 1345.

[4] *Ann. Chem. Pharm.* cxxxiii. 321.

[5] *Ibid.* ciii.

Salicylsulphuric acid, $C_6H_4(SO_4H)CO_2H$. The potassium salt may be obtained by heating salicylic acid with caustic potash and potassium disulphate; it crystallizes in colourless, pointed prisms and is readily soluble in water, but insoluble in absolute alcohol. It gives no colouration with ferric chloride and is decomposed by dilute acids, including even acetic acid, into potassium sulphate and salicylic acid.[2]

Diazosalicylic acid,  $C_6H_3(OH)\begin{cases} N{=}N \\ CO.O \end{cases}$, is formed by passing nitrogen trioxide into an alcoholic solution of the hydrochloride of amidosalicylic acid. It crystallizes in fine needles and combines with acids to form salts which crystallize well;[3] iodosalicylic acid is formed on heating with hydriodic acid.

Azobenzenesalicylic acid, $C_6H_5.N_2.C_6H_3(OH)CO_2H$, is obtained by the action of diazobenzene nitrate on an alkaline solution of salicylic acid; it crystallizes in orange-red needles, which are insoluble in water, but dissolve readily in alcohol. Sulphuric acid converts it into a sulphonic acid, which is probably identical with the following compound.[4]

Salicylparazobenzenesulphonic acid, $C_6H_4(SO_3H)N_2.C_6H_3(OH)CO_2H$, is formed by bringing salicylic acid into a solution of paradiazobenzenesulphonic acid in caustic potash. It crystallizes in golden-yellow needles, which are only slightly soluble in hot water; barium chloride produces a yellow precipitate of $(C_{13}H_9N_2SO_6)_2Ba$, which is converted on boiling into irregular, six-sided, lustrous plates.[5]

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[1] Remsen, *Ann. Chem. Pharm.* clxxix. 107.

[2] Baumann, *Ber. Deutsch. Chem. Ges.* xi. 1914.

[3] Schmitt, *Jahresber. Chem.* 1864, 384; Schmidt and Mittenzwey, *Journ. Prakt. Chem.* [2] xviii. 193; Goldberg, *ibid.* xix. 362.

[4] Stebbins, *Ber. Deutsch. Chem. Ges.* xiii. 716.

[5] Griess, *ibid.* xi. 2196.

METAHYDROXYBENZOIC ACID.

[illegible] Gerland obtained this isomeride of salicylic acid by the action of nitrous acid on a hot solution of ordinary amidobenzoic acid and gave it the name of oxybenzoic acid,[1] by which it is still generally designated. It is also formed by fusing sulphobenzoic acid[2] metachlorobenzoic acid,[3] or metachlorocresol[4] with caustic potash.

In order to prepare it 2 parts of potassium sulphobenzoate are fused with 3 parts of caustic potash and a little water, the melt acidified with sulphuric acid and the whole extracted with ether.

The metahydroxybenzoic acid is left on evaporation in thick, white crusts which are purified by re-crystallization from hot water. Any adhering benzoic acid is finally removed by washing with carbon disulphide (Barth).

Metahydroxybenzoic acid crystallizes in small prisms or needles melting at 200°, which usually form warty aggregates. It dissolves at 0° in 265, and at 18° in 108·2 parts of water, has a sweet taste, is not coloured by ferric chloride and can be distilled without undergoing decomposition. It differs from its isomerides in being reduced by sodium amalgam in an acid solution to metahydroxybenzyl alcohol, and in blackening at 300° without a trace of phenol being formed; decomposition, accompanied by the formation of small quantities of the latter, only occurs at higher temperatures.[5]

The Metahydroxybenzoates. The salts of the alkali metals are readily soluble and do not crystallize well; they are very stable and only decompose at a high temperature, very little phenol and no isomeric acid being formed. The basic salts do not combine with carbon dioxide at a high temperature (Kupferberg); when the acid is fused with an excess of sodium carbonate, decomposition sets in above 300°, the greater portion of the acid being completely burnt, and only a small quantity of phenol being therefore formed.[6] If two molecules of the acid are heated to 350° with three molecules of caustic baryta, no change takes place, but if seven molecules of the latter be employed, a complete decomposition into carbon dioxide and phenol occurs (Klepl).

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[1] *Ann. Chem. Pharm.* lxxxvi. 143; xci. 189; Fischer, *ibid.* cxxvii. 138.

[2] Barth, *ibid.* cxlviii. 30.

[3] Dembey, *ibid.* cxlviii. 222.

[4] Barth, *ibid.* cliv. 361.

[5] Klepl, *Journ. Prakt. Chem.* [2] xxv. 464; xxvii. 159.

[6] Barth and Schreder, *Ber. Deutsch. Chem. Ges.* xii. 1254.

Ammonium metahydroxybenzoate, $C_6H_4(OH)CO_2NH_4$, crystallizes in needles which form fascicular aggregates.

Calcium metahydroxybenzoate, $(C_6H_4.OH.CO_2)_2Ca + 3H_2O$, forms readily soluble crystals.

Barium metahydroxybenzoate, $(C_6H_4.OH.CO_2)_2Ba$, is an amorphous, gummy mass; it has been found impossible to prepare a basic salt.

Copper metahydroxybenzoate, $(C_6H_4.OH.CO_2)_2Cu+H_2O$, crystallizes from hot water in greenish needles.

Thallium metahydroxybenzoate, $C_6H_4(OH)CO_2Tl$, is prepared by neutralizing a hot solution of the acid with thallium carbonate; it crystallizes on cooling in lustrous, colourless prisms. When a solution of the hydroxide is neutralized with the acid and an equal quantity of the hydroxide added to the neutral solution, the basic salt, $C_6H_4(OTl)CO_2Tl$, crystallizes on evaporation in yellowish prisms; it is more readily soluble than the normal salt and has an alkaline reaction (Kupferberg).

The methylamine salt decomposes into its constituents when heated, and the aniline salt behaves in a similar manner, a little hydroxybenzanilide being also formed, while tetra-ethylammonium metahydroxybenzoate splits up into tri-ethylamine and ethyl metahydroxybenzoate.

Ethyl metahydroxybenzoate, $C_6H_4(OH)CO_2.C_2H_5$, is formed by the action of hydrochloric acid gas on an alcoholic solution of the acid,[1] or by heating the normal potassium salt with ethyl iodide.[2] It crystallizes from ether in tablets, melts at 72°, boils at 282°, and is converted by caustic soda into a crystalline mass of $C_6H_4(ONa)CO_2.C_2H_5$, which is readily soluble in water and alcohol.

Metamethoxybenzoic acid, $C_6H_4(OCH_3)CO_2H$, is obtained by heating metahydroxybenzoic acid with the calculated quantity of caustic potash and methyl iodide, and decomposing the ethereal salt thus formed with a solution of caustic potash in wood-spirit (Gräbe and Schultzen). It is also formed by the oxidation of metacresyl methyl ether with potassium permanganate,[3] and by

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[1] Gräbe and Schultzen, *Ann. Chem. Pharm.* cxlii. 351.
[2] Heintz, *ibid.* cliii. 337.
[3] Oppenheim and Pfaff, *Ber. Deutsch. Chem. Ges.* viii. 887.

[illegible]

[illegible] was prepared by [illegible]

[illegible] is obtained [illegible]

[illegible] is prepared [illegible]

[illegible]

converted by water into metacarboxyphenylphosphoric acid, while on heating with phosphorus pentachloride to 180°, a portion is converted into metachlorobenzenyl trichloride.[1]

Metahydroxybenzamide, $C_6H_4(OH)CO.NH_2$, is formed when diazobenzamide nitrate is boiled with water[2] as well as by the action of ammonia on ethyl metahydroxybenzoate. It crystallizes from water in thin plates, which have a bitter taste and melt at 167°.

Metahydroxybenzanilide, $C_6H_4(OH)CO.NH(C_6H_5)$, is obtained in the same way as salicylanilide; it crystallizes from dilute alcohol in needles, melting at 154°—155°, and combines with alkalis to form salts which crystallize well. It is not attacked by boiling alkalis, but is decomposed by them on fusion (Kupferberg).

Metahydroxybenzuric acid, $C_6H_4(OH)CO.NH.CH_2.CO_2H$, occurs in the urine of the dog after metahydroxybenzoic acid has been administered; it crystallizes in needles.[3]

Metahydroxybenzonitril, $C_6H_4(OH)CN$, is formed by boiling diazobenzonitril sulphate with water[4] and by heating metahydroxybenzoic acid in a current of ammonia, first to 220°—230° and then to 300°—320°; the isomeric compounds are decomposed by this treatment into phenol and carbon dioxide, but yield no nitril.[5] Metahydroxybenzonitril crystallizes from hot water in small plates and from alcohol in small, rhombic prisms; it has an intensely sweet and at the same time sharp taste, melts at 82°, and decomposes on heating with hydrochloric acid into ammonia and metahydroxybenzoic acid.

SUBSTITUTION PRODUCTS OF METAHYDROXYBENZOIC ACID.

2182 *Iodometahydroxybenzoic acid*, $C_6H_3I(OH)CO_2H$. Weselsky obtained this substance by the action of iodine and mercuric oxide on an alcoholic solution of metahydroxybenzoic acid. It crystallizes in needles, which are only slightly soluble in cold water.

Nitrometahydroxybenzoic acids, $C_6H_3(NO_2)(OH)CO_2H$. Gerland found that the direct nitration of metahydroxybenzoic acid yields a nitrohydroxybenzoic acid, which forms yellow, rhombic crystals, and has a repulsive bitter taste; it must be identical with one of those described below, since metahydroxybenzoic acid can only yield four mononitro-derivatives. The first three were prepared by Griess by boiling the corresponding nitro-amidobenzoic acids with caustic potash.[1]

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[1] Anschütz, private communication.

[2] Griess, *Zeitschr. Chem.* 1866, 1.

[3] Baumann and Heiter, *Hoppe-Seyler's Zeitschrift*, i. 260.

[4] Griess, *Ber. Deutsch. Chem. Ges.* viii. 859.

[5] Smith, *Journ. Prakt. Chem.* [2] xvi. 218.

α-Nitrometahydroxybenzoic acid, ($CO_2H : OH : NO_2 = 1 : 3 : 6$), is readily soluble in water, and crystallizes in thick, honey-yellow prisms or in needles containing one molecule of water, which is given off at a few degrees above 100°. It melts at 169°, has a slightly acid taste, and is coloured a faint reddish brown by ferric chloride. The barium salt, $C_7H_3NO_5Ba + 6H_2O$, forms yellowish red prisms, which are readily soluble in water.

β-Nitrometahydroxybenzoic acid (1 : 3 : 4), is slightly soluble in hot water, and crystallizes in long, yellow, four- or six-sided plates, melting at 230°. The barium salt, $C_7H_3NO_5Ba + H_2O$, is almost insoluble and crystallizes in yellowish red plates.

γ-Nitrometahydroxybenzoic acid (1 : 3 : 2),is less soluble in water than the *α*-acid, has an intensely sweet taste, and crystallizes with one molecule of water in long, four-sided plates or large tablets, which melt at 178° and give a faint reddish brown colouration with ferric chloride. The barium salt, $2C_7H_3NO_5Ba + 3H_2O$, also has a very sweet taste, and forms tolerably soluble reddish brown plates.

η-Nitrometahydroxybenzoic acid (1 : 3 : 5), was prepared by Grube from the corresponding nitro-amidobenzoic acid,[2] and is a yellowish brown, crystalline precipitate. Its salts crystallize badly.

Trinitrometahydroxybenzoic acid, $C_6H(NO_2)_3(OH)CO_2H$, is formed by heating diazo-amidobenzoic acid with ordinary strong nitric acid,[3] and by the action of fuming nitric acid on metamidobenzoic acid.[4] It crystallizes in large, almost colourless, rhombic prisms, which have a vitreous lustre, and are best obtained from solution in concentrated nitric acid; it is readily dissolved by water, alcohol, and ether, forming intensely yellow solutions, which dye animal fabrics in the same way as picric acid. It melts when heated and then explodes.

The barium salt, $C_7HN_3O_9Ba + 3H_2O$, is tolerably soluble in water, but insoluble in alcohol, and crystallizes in thick, light yellow needles, which are very explosive.

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[1] *Ber. Deutsch. Chem. Ges.* xi. 1729.

[2] *Ibid.* x. 1704

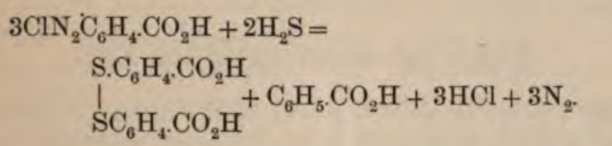
[3] Griess, *Ann. Chem. Pharm.* cxvii. 28.

[4] Beilstein and Geitner, *ibid.* cxxxix. 11

When metahydroxybenzoic acid is heated with sulphuric acid, three compounds isomeric with alizarin, $C_{14}H_8O_4$, are formed.[1] If the product be boiled with strong nitric acid, a trinitrometahydroxybenzoic acid is produced among other products, which is readily soluble in water, and crystallizes in tablets or prisms containing one molecule of water, which is lost at 100°. It melts at 105° and then commences to sublime; when rapidly heated it detonates. The barium salt, $C_7HN_3O_9Ba + 2H_2O$, is readily soluble in water, and crystallizes in yellow needles, which explode at 299°.[2]

Thiometahydroxybenzoic acid, $C_6H_4(SH)CO_2H$, is formed by the action of tin and hydrochloric acid on sulphobenzoyl chloride, $C_6H_4(SO_2Cl)COCl$. It is tolerably soluble in water, more readily in alcohol, and sublimes very easily in small plates, melting at 146°—147°.

Dithiometahydroxybenzoic acid, $S_2(C_6H_4.CO_2H)_2$, is obtained by exposing the monothio-compound to the air in the moist state, or more rapidly by adding bromine water to its aqueous solution.[3] Griess prepared it by decomposing diazobenzoic acid aurichloride with sulphuretted hydrogen:[4]



$$3ClN_2C_6H_4.CO_2H + 2H_2S = \begin{array}{l} S.C_6H_4.CO_2H \\ | \\ SC_6H_4.CO_2H \end{array} + C_6H_5.CO_2H + 3HCl + 3N_2.$$

It crystallizes in microscopic needles, which are scarcely soluble in water, more readily in alcohol, and melt at 242°—244°.

Sulphometahydroxybenzoic acid, $C_6H_3(SO_3H)(OH)CO_2H$, is formed by the action of sulphur trioxide on metahydroxybenzoic acid; it crystallizes in green, deliquescent needles, melting at 208°, is almost insoluble in ether and is coloured wine-red by ferric chloride.[5]

Isosulphometahydroxybenzoic acid is obtained by dissolving the sulphate of diazobenzoic acid in warm sulphuric acid; it crystallizes in plates, which are readily soluble in water and alcohol. It is decomposed by strong nitric acid into trinitrometahydroxybenzoic acid and sulphuric acid.[6]

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[1] Schunck and Römer, *Ber. Deutsch. Chem. Ges.* xi. 1167.

[2] Schardinger, *ibid.* viii. 1490.

[3] Hübner and Upmann, *Zeitschr. Chem.* 1870, 294; Frerichs, *Ber. Deutsch. Chem. Ges.* vii. 793.

[4] *Journ. Prakt. Chem.* [2] i. 102.

[5] Barth, *Ann. Chem. Pharm.* cxlviii. 38; Senhofer, *ibid.* clii. 102.

[6] Griess, *Jahresber. Chem.* 1864, 351.

Disulphometahydroxybenzoic acid, $C_6H_2(SO_3H)_2(OH)CO_2H$, seems to be formed when metahydroxybenzonitril is heated with fuming sulphuric acid;[1] its barium salt is obtained by boiling the following compound with baryta water.[2]

Trisulphometahydroxybenzoic acid, $C_6H(SO_3H)_3(OH)CO_2H$, is obtained by heating metahydroxybenzoic acid to 250° with a mixture of fuming sulphuric acid and phosphorus pentoxide. The free acid is a honey-yellow syrup; it is coloured an intense carmine-red by ferric chloride, and on fusion with caustic potash undergoes complete oxidation.

Metahydroxybenzoylsulphuric acid, $C_6H_4(SO_4H)CO_2H$, is found in the urine of men and dogs after the administration of metahydroxybenzoic acid (Baumann and Heiter). Its potassium salt is obtained in a similar manner to that of salicylsulphuric acid; it forms deliquescent needles, and decomposes on boiling with hydrochloric acid or alcoholic potash into metahydroxybenzoic acid and sulphuric acid.[3]

PARAHYDROXYBENZOIC ACID.

2183 Fischer obtained this acid by the action of nitrous acid on an aqueous solution of paramidobenzoic acid,[4] and Saytzew by heating anisic acid (methylparahydroxybenzoic acid) with hydriodic acid.[5] It is also formed when para-compounds such as anisic acid,[6] paracresol,[7] parasulphobenzoic acid,[8] &c., are fused with caustic potash; it may be obtained by the same method from various resins, as gum benzoin, dragon's blood, aloes and acaroïd resin.[9]

Kolbe prepared it synthetically by adding potassium to boiling phenol and at the same time passing in carbon dioxide; parahydroxybenzoic acid alone is formed, while if the temperature be not allowed to rise above 130°—150°, salicylic acid is obtained.

Parahydroxybenzoic acid may also be prepared by the action of carbon dioxide on potassium phenate at 170°—210°;[1] it is formed in small quantities, together with salicylic acid, when sodium phenate is treated in a similar manner at a lower temperature.[2] The fact that normal potassium salicylate decomposes at 220° into carbon dioxide, phenol and basic potassium parahydroxybenzoate, has been already mentioned. Parahydroxybenzoic acid is further obtained, together with a smaller quantity of salicylic acid,[3] by heating tetrachloromethane to 100° with phenol and alcoholic soda.[4]

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[1] Smith, *Journ. Prakt. Chem.* [2] xvi. 229.
[2] Kretschy, *Ber. Deutsch. Chem. Ges.* xi. 858.
[3] Baumann, *ibid.* xi. 1915.
[4] *Ann. Chem. Pharm.* cxxvii. 129.
[5] *Ibid.* cxxvii. 145.
[6] Barth, *Zeitschrift. Chem.* 1866, 650.
[7] Barth, *Ann. Chem. Pharm.* cliv. 359.
[8] Remsen, *ibid* clxxviii. 281.
[9] Barth and Hlasiwetz, *ibid.* cxxxiv. 274; cxxxix. 78.

It is formed in theoretical amount when the potassium salt of paracresylsulphuric acid is oxidized with potassium permanganate in alkaline solution.[5] Paracresol is also converted into parahydroxybenzoic acid in passing through the animal organism, while metacresol is found in the urine as metacresylsulphuric acid, and orthocresol is partly converted into orthocresylsulphuric acid and partly into hydrotoluquinone.[6]

In order to prepare parahydroxybenzoic acid, a mixture of equal molecules of caustic potash and phenol is heated in a current of hydrogen, the temperature being finally raised to 180°; carbon dioxide is then passed in until the theoretical quantity of phenol has distilled over, and the residue is then dissolved in water and decomposed by hydrochloric acid. The parahydroxybenzoic acid is boiled with animal charcoal and crystallized from hot water. It is thus obtained in small, monoclinic prisms, while it is deposited from dilute alcohol in larger crystals,[7] containing one molecule of water, which is lost at 100°; it dissolves in 580 parts of water at 0°, and in 126 parts at 15°, and is readily soluble in hot water, alcohol and ether, but only slightly in chloroform, which is therefore employed to free it from salicylic acid. Its slight solubility in carbon disulphide is made use of in separating it from benzoic acid. It melts at 200° and when rapidly heated decomposes partly into carbon dioxide and phenol, and partly into other products, which will be described below. It decomposes completely and readily into phenol and carbon dioxide on heating with dilute sulphuric acid in a sealed tube.[8] Its aqueous solution gives an amorphous, yellow precipitate with ferric chloride. Phosphorus pentachloride converts it into parachlorobenzoyl chloride.

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[1] Kolbe, *Journ. Prakt. Chem.* [2] x. 100.
[2] Ost, *ibid.* [2] xx. 208.
[3] Hasse, *Ber. Deutsch. Chem. Ges.* ix. 2186.
[4] Reimer and Tiemann, *ibid.* ix. 1285.
[5] Heymann and Königs, *ibid.* xix. 704.
[6] Baumann and Preusse, *ibid.* xix. 706.
[7] Hartmann, *Journ. Prakt. Chem.* [2] xvi. 35.
[8] Klepl, *ibid.* [2] xxv. 464.

The Parahydroxybenzoates. The normal sodium salt decomposes completely at 240°—250° into carbon dioxide, phenol and the basic salt; when, however, it is heated to 280°—295° in a current of carbon dioxide, salicylic acid is obtained, while both hydroxyisophthalic acid and hydroxytrimesic acid are formed at temperatures above 340° (Kupferberg). When, on the other hand, the acid is heated with eight to ten parts of caustic soda, a partial decomposition into phenol and carbon dioxide sets in at 355° (Barth and Schreder), The salts of methylamine and aniline decompose at a higher temperature into phenol, carbon dioxide and the base, while that of tetra-ethylammonium decomposes on distillation into tri-ethylamine and ethyl parahydroxybenzoate, the latter of which is then partially resolved into carbon dioxide and phenetol.

Sodium parahydroxybenzoate, $C_6H_4(OH)CO_2Na + 5H_2O$, crystallizes from concentrated solutions in transparent tablets, which effloresce in the air.

Potassium parahydroxybenzoate, $C_6H_4(OH)CO_2K + 3H_2O$, is similar to the sodium salt, but is stable in the air.

Ammonium parahydroxybenzoate, $C_6H_4(OH)CO_2NH_4 + H_2O$, crystallizes in long prisms.

Calcium parahydroxybenzoate, $(C_7H_5O_3)_2Ca + 4H_2O$, forms fine needles grouped in stellate forms, and is very soluble.

Barium parahydroxybenzoate, $(C_7H_5O_3)_2Ba + H_2O$, crystallizes in flat, lustrous needles or with two molecules of water in pointed rhombohedra; baryta water added to its solution produces a precipitate of the basic salt, $C_7H_4O_3Ba$, as a sandy, crystalline powder, which is scarcely soluble in cold water.

Lead parahydroxybenzoate, $(C_7H_5O_3)_2Pb + 2H_2O$, is a very characteristic salt, and is obtained by neutralizing the boiling aqueous solution of the acid with lead carbonate. It separates out on cooling in thin, iridescent plates which take a silver lustre on drying, and resemble those of benzoic acid.

Copper parahydroxybenzoate, $(C_7H_5O_3)_2Cu + 6H_2O$, crystallizes in small, bluish green needles, which become dull and insoluble on boiling with water.

Silver parahydroxybenzoate, $C_7H_5O_3Ag + 2H_2O$, crystallizes from hot water in small, lustrous plates.

Methyl parahydroxybenzoate, $C_6H_4(OH)CO_2CH_3$, is formed by heating together equal molecules of parahydroxybenzoic acid, caustic potash and methyl iodide; it crystallizes from ether in large tablets, melts at 17° and boils at 283°.[1]

2184 *Paramethoxybenzoic acid,* or *Anisic acid,* $C_6H_4(OCH_3)CO_2H$. Cahours obtained this compound in 1839 by the oxidation of oil of anise-seed, and showed at the same time that it is formed from the "camphor" (anethol or allylphenol, $C_6H_4(OH)C_3H_5$), contained in this substance.[2] Laurent, in 1841, prepared from tarragon oil (from *Artemisia dracunculus*), the so-called dragonic acid (*acide draconique*), which, according to Gerhardt, is identical with anisic acid. This view was subsequently confirmed by Laurent, who also accurately determined its composition.[3]

At about the same time Persoz submitted oil of anise-seed, fennel oil, and star-anise oil (*huile de badiane*, from *Illicium anisatum*) to oxidation, and obtained two acids, which he named umbellic acid (*acide ombellique*) and badianic acid (*acide badianique*).[4] Hempel showed, however, that these are both anisic acid,[5] the formation of which might have been expected, since the oils employed contain anethol.[6]

Anisic acid was at first looked upon as the homologue of salicylic acid; Kolbe, however, considered it to be methoxybenzoic acid, since it behaves very similarly to benzoic acid, and decomposes into anisol (phenyl methyl ether) and carbon dioxide when distilled with caustic baryta.[7]

In order to determine from which of the hydroxybenzoic acids it is derived, Saytzew heated it with hydriodic acid, and found that the product consists of parahydroxybenzoic acid. It was then thought probable that anisic acid and winter-green oil would have similar constitutions, but Gräbe showed that the latter is the methyl ether of salicylic acid, while Ladenburg proved that in anisic acid the methyl group replaces the hydrogen of the phenol hydroxyl; by heating equal molecules of potassium parahydroxybenzoate and caustic potash with two molecules of methyl iodide, he obtained the methyl ether of paramethoxybenzoic acid (anisic acid) and prepared the free acid by saponifying with potash and decomposing the product with hydrochloric acid.[8] Anisic acid may also be obtained by oxidizing orthocresyl methyl ether with chromic acid solution.[9]

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[1] Ladenburg and Fitz, *Ann. Chem. Pharm.* cxli. 247.

[2] *Ibid.* xli. 66.

[3] *Ibid.* xliv. 313.

[4] *Ibid.* xliv. 311.

[5] *Ibid.* lix. 104.

[6] Cahours, *ibid.* xxxv. 312.

[7] *Lehrb. d. Organ. Chem.* ii. 135.

[8] *Ann. Chem. Pharm.* cxli. 241.

[9] Körner, *Zeitschr. Chem.* 1868, 326.

In order to prepare it, 1 part of oil of anise seed is poured into a solution of 5 parts of potassium dichromate in 10 parts of sulphuric acid and 20 parts of water, which is heated to 50°. The reaction is completed in a few minutes and the solution is then allowed to cool, the anisic acid filtered off and purified by precipitation with hydrochloric acid from solution in ammonia (Ladenburg and Fitz).

It crystallizes in long monoclinic prisms or needles, melting at 184°, which dissolve in 2500 parts of water at 18°. It is tolerably soluble in boiling water and very readily in alcohol. On heating with hydriodic or concentrated hydrochloric acid, or on fusion with potash, it is converted into parahydroxybenzoic acid.

Its salts, which crystallize well, have been chiefly investigated by Engelhardt and by Borella.[1]

	Melting-point.	Boiling-point.
Methyl paramethoxybenzoate,[2] $C_6H_4(OCH_3)CO_2CH_3$, scales . .	45°—46°	255°
Ethyl paramethoxybenzoate,[3] $C_6H_4(OCH_3)CO_2C_2H_5$, liquid . .	—	250°—255°
Ethyl parahydroxybenzoate,[4] $C_6H_4(OH)CO_2C_2H_5$, crystals . .	116°	297°—298°
Para-ethoxybenzoic acid,[5] $C_6H_4(OC_2H_5)CO_2H$, needles . .	195°	—
Ethyl para-ethoxybenzoate,[6] $C_6H_4(OC_2H_5)CO_2C_2H_5$, liquid . .	--	275°

Paracetoxybenzoic acid, $C_6H_4(OCO.CH_3)CO_2H$, is formed when parahydroxybenzoic acid is heated with acetic anhydride. It is slightly soluble in water, and crystallizes from chloroform in large plates, which have a silver lustre and melt at 185° (Klepl).

Phenyl parahydroxybenzoate, $C_6H_4(OH)CO_2.C_6H_5$, occurs in the products which are formed by the dry distillation of the acid. It is insoluble in water, but readily soluble in alcohol and chloroform, from which it crystallizes in compact, rhombic tablets, which melt at 176°, dissolve readily in caustic soda, and are decomposed by it even in the cold with formation of phenol and parahydroxybenzoic acid (Klepl).

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[1] *Gaz. Chim. Ital.* xv. 304; *Ann. Chem. Pharm.* cviii. 240.

[2] Ladenburg and Fitz, *ibid.* cxli. 252.

[3] Cahours, *ibid.* lvi. 310.

[4] Grabe, *ibid.* cxxxix. 146; Hartmann, *Journ. Prakt. Chem.* [2] xvi. 50.

[5] Ladenburg and Fitz; Fuchs, *Ber. Deutsch. Chem. Ges.* ii. 624.

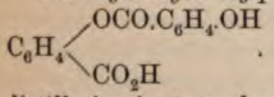
[6] Ladenburg and Fitz.

Paraphenoxybenzoic acid, $C_6H_4(OC_6H_5)CO_2H$, is obtained by boiling the following compound with alcoholic potash, or by heating it to 200° with concentrated hydrochloric acid. It is readily soluble in alcohol and ether, and crystallizes from chloroform in long prisms melting at 159·5°. When heated with caustic baryta it decomposes into carbon dioxide and diphenyl ether.

Phenyl paraphenoxybenzoate, $C_6H_4(OC_6H_5)CO_2.C_6H_5$, is formed when parahydroxybenzide, which is described below, is heated to about 400°, preferably in a current of carbon dioxide. It crystallizes from dilute alcohol in fatty scales, which melt at 73°—78°, and sublime at a higher temperature, forming a vapour which smells like the geranium.

2185 *Anhydrides of parahydroxybenzoic acid.* When parahydroxybenzoic acid is submitted to dry distillation, only half of it is decomposed into carbon dioxide and phenol, which distils over accompanied by water, and phenyl parahydroxybenzoate; as the distillation is continued, the boiling acid suddenly becomes turbid, and a milky liquid settles in the retort, until at 350° the residue solidifies to a white amorphous mass.[1]

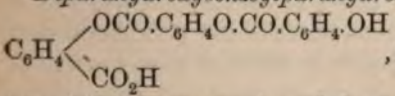
Parahydroxybenzoylparahydroxybenzoic acid,



$$C_6H_4\begin{cases}OCO.C_6H_4.OH\\CO_2H\end{cases}$$

. In order to prepare this compound, the distillation is stopped as soon as the acid has lost about 15 per cent. of its weight and before any turbidity has appeared. The residue is boiled with chloroform and water, and the compound then extracted with dilute alcohol and purified by re-crystallization. It forms short, microscopic needles, which melt at 261° and are rapidly converted into parahydroxybenzoic acid in alkaline solution. As a monobasic acid it forms a barium salt, $(C_{14}H_9O_5)_2Ba$, which crystallizes in long plates containing water of crystallization. On heating with acetic anhydride, the monoacetyl compound, $C_{14}H_9(C_2H_3O)O_5$, is formed; it crystallizes in small plates, melting at 216·5°.

Diparahydroxybenzoylparahydroxybenzoic acid,



$$C_6H_4\begin{cases}OCO.C_6H_4O.CO.C_6H_4.OH\\CO_2H\end{cases}$$

, is contained in the residue obtained in the preparation of the preceding compound, and also in the amorphous mass formed by the distillation of parahydroxybenzoic acid, from which it may be extracted by absolute alcohol. It is a white, non-crystalline powder, which is slightly soluble in alcohol and ether, but insoluble in water and chloroform; it melts at 280°, and readily dissolves in alkalis, being gradually converted into parahydroxybenzoic acid, while it is not altered by boiling water. When the acid is suspended in a small quantity of water and treated with sufficient caustic soda to effect solution, the compound $C_{21}H_{13}O_7Na$ is precipitated in needles after some time. The acetyl compound, $C_{21}H_{13}(C_2H_3O)O_7$, is formed by heating the acid with acetic acid; it crystallizes in needles melting at 230°.

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[1] *Klepl, Journ. Prakt. Chem.* [2] xxv. 525; xxviii. 193.

Parahydroxybenzide, $(C_7H_4O_2)_n$, is the final product of the action of heat upon parahydroxybenzoic acid, and forms a white, amorphous powder, which is insoluble in the ordinary solvents, and carbonizes at 350° without previously melting. Boiling concentrated caustic potash converts it into parahydroxybenzoic acid; on heating with concentrated sulphuric acid, parahydroxybenzoylsulphuric acid is obtained, while parachlorobenzenyl trichloride is formed by the action of phosphorus chloride at 300° (p. 196).

Anisic anhydride, $(C_6H_4(OCH_3)CO)_2O$, is obtained by the action of phosphorus oxychloride on sodium anisate. It crystallizes from ether in small, silky needles, which melt at 99° and volatilize at a higher temperature without decomposition.[1]

Methylparahydroxybenzoyl chloride, or *Anisyl chloride*, $C_6H_4(OCH_3)COCl$, is formed by the action of phosphorus pentachloride on anisic acid.[2] It forms long needles, which cannot be volatilized.[3]

Paracarbonylphenylphosphoryl chloride, $C_6H_4(OPOCl_2)COCl$, is prepared by the action of phosphorus pentachloride on dehydrated parahydroxybenzoic acid, the reaction being more violent than in the case of salicylic or metahydroxybenzoic acids. It boils at 176° under a pressure of 13—14 mm., and is a powerfully refractive liquid. Water converts it into *paracarbonylorthophosphoric acid*, $C_6H_4(CO_2H)PO(OH)_2$, which crystallizes in fine, white plates, melting at 200°; it is only decomposed by water at 150°—160°, parahydroxybenzoic and phosphoric acids being formed. When the chloride is distilled slowly under the ordinary pressure, it passes over almost unaltered, only a small portion decomposing into phosphorus oxychloride and parachlorobenzoyl chloride.

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[1] Pisani, *Ann. Chem. Pharm.* cii. 284.

[2] Cahours, *ibid.* lxx. 47.

[3] Lossen, *ibid.* clxxv. 284.

The behaviour of this chloride towards a second molecule of phosphorus pentachloride is of considerable interest, since it differs from that of its isomerides inasmuch as no parabenzenyltrichlorophosphoryl chloride is formed, but the compound decomposes into phosphorus oxychloride and parachlorobenzoyl chloride, the latter being then partially converted into parachlorobenzenyl trichloride. The phenol-oxygen is therefore more readily replaced by chlorine when it occupies the para-position than when it is present in either an ortho- or meta-disubstituted compound.[1]

Parahydroxybenzamide, $C_6H_4(OH)CO.NH_2+H_2O$, is obtained by heating the ethyl ether with ammonia under pressure. It crystallizes from hot water in strongly lustrous, rhombic needles, which lose their water of crystallization at 100° and then melt at 162.°

Anisamide, $C_6H_4(OCH_3)CO.NH_2$, was prepared by Cahours from the chloride by the action of ammonia; it crystallizes in prisms, melts at 137°—138°, sublimes in broad plates and boils at 295° (Henry).

Parahydroxybenzanilide, $C_6H_4(OH)CO.NH(C_6H_5)$, is formed when the acid is heated with aniline and the product treated with phosphorus trichloride. It crystallizes from hot water in yellowish, lustrous plates, melting at 196°—197°. It forms salts of potassium and sodium, which are readily soluble and crystallize well (Kupferberg).

Anisanilide, $C_6H_4(OCH_3)CO.NH(C_6H_5)$, was obtained by Lossen as a product of the distillation of benzanishydroxamic acid (p. 340). It is slightly soluble in cold alcohol, and crystallizes in rhombic plates, melting at 168°—169°.

Parahydroxybenzuric acid, $C_6H_4(OH)CO.NH.CH_2.CO_2H$, appears, together with parahydroxybenzoylsulphuric acid, in the urine of the dog after the administration of parahydroxybenzoic acid; it crystallizes in short prisms, which are tolerably soluble in water (Baumann and Heiter).

Anisuric acid, $C_6H_4(OCH_3)CO.NH.CH_2.CO_2H$, was obtained by Cahours from silver amido-acetate and anisyl chloride,[2] and is also found in the urine after anisic acid has been taken;[3] it forms foliaceous crystals, which are readily soluble in hot water.

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[1] Anschütz, private communication.
[2] *Ann. Chem. Pharm.* cix. 32.
[3] Gräbe and Schultzen, *ibid.* cxlii. 348.

Parahydroxybenzonitril, $C_6H_4(OH)CN$, is formed when ammonium parahydroxybenzoate mixed with phosphorus pentoxide is distilled in a current of carbon dioxide (Hartmann), and by the action of ammonia on parahydroxybenzide mixed with pumice-stone and heated to 250° (Klepl). It crystallizes from hot water in rhombic tablets, which melt at 113°, and have a sweet but pungent taste; it forms a series of salts in which the phenol-hydrogen is replaced by the metal.

Anisonitril, $C_6H_4(OCH_3)CN$. Henry obtained this substance by distilling the amide with phosphorus pentachloride. It crystallizes from hot water in small needles, and from ether in long, white, lustrous prisms, has a penetrating, characteristic rank odour, melts at 56°—57°, and boils at 253°—254°.[1]

SUBSTITUTION PRODUCTS OF PARAHYDROXYBENZOIC ACID.

2186 *Chloroparahydroxybenzoic acid*, $C_6H_3Cl(OH)CO_2H$, (3:4:1), is formed by heating parahydroxybenzoic acid with antimony pentachloride,[2] and by the action of alcoholic potash on orthochlorophenol at 125°—136°.[3] It is slightly soluble in cold, more readily in hot water, and crystallizes in small needles, which melt at 169°—170°, and sublime without decomposition. Ferric chloride produces a brown precipitate in a concentrated solution; phosphorus pentachloride converts it into the chloride of α-dichlorobenzoic acid (Lössner).

Dichloroparahydroxybenzoic acid, $C_6H_2Cl_2(OH)CO_2H$, has also been prepared by Lössner; it crystallizes in fine needles, which melt at 255°—256°.

Dibromoparahydroxybenzoic acid, $C_6H_2Br_2(OH)CO_2H$, (3:5:4:1), has been obtained from dibromanisic acid. It is scarcely soluble in water, and crystallizes from alcohol in needles, which melt with decomposition at 266°—268°, but sublime at a lower temperature. A monobromoparahydroxybenzoic acid is not known; when bromine water is added to a solution of parahydroxybenzoic acid, a precipitate of tribromophenol is produced (Barth and Hlasiwetz).

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[1] *Ber. Deutsch. Chem. Ges.* ii. 666.
[2] Lössner, *Journ. Prakt. Chem.* [2] xiii. 432.
[3] Hasse, *Ber. Deutsch. Chem. Ges.* x. 2192.

Iodoparahydroxybenzoic acid, $2C_6H_3I(OH)CO_2H + H_2O$, is formed when parahydroxybenzoic acid is boiled with water, iodine and iodic acid; it crystallizes from hot water in small needles, which become anhydrous at 100° and then melt at 192°.[1]

Di-iodoparahydroxybenzoic acid, $C_6H_2I_2(OH)CO_2H$, is formed together with the preceding compound, and crystallizes in small needles, which are scarcely soluble in water, but readily in alcohol.

Nitroparahydroxybenzoic acid, $C_6H_3(NO_2)(OH)CO_2H$, (3 : 4 : 1). Griess obtained this compound by the action of boiling potash on δ-nitro-amidobenzoic acid.[2] It is also formed in small quantity, together with β-nitro-salicylic acid, by heating orthonitrophenol with alcoholic potash and tetrachloromethane (Hasse). It crystallizes from boiling water in yellowish needles, melting at 185°. Its solution is not coloured by ferric chloride.

Basic barium nitroparahydroxybenzoate, $C_7H_3NO_5Ba + H_2O$, is obtained by adding barium chloride to a hot, ammoniacal solution of the acid. It forms yellowish red, lustrous plates.

Dinitroparahydroxybenzoic acid, $C_6H_2(NO_2)_2(OH)CO_2H$, (3 : 5 : 1 : 4) is formed when a boiling solution of dinitroparamidobenzoic acid is treated with nitrous acid or with caustic potash. It is slightly soluble in cold, more readily in hot water, and crystallizes in large, thin tablets, which are coloured light yellow to bronze, and melt at 235°—237°.[3]

Its salts are coloured yellow or orange-red, and crystallize well.

Barth has prepared a mono- and a di- nitro-acid by the action of nitric acid on parahydroxybenzoic acid, both of which seem to be different from the preceding compounds.

Amidoparahydroxybenzoic acid, $C_6H_3(NH_2)(OH)CO_2H$. Barth obtained this substance bythe reduction of his nitroparahydroxybenzoic acid. It crystallizes in needles and forms a sulphate which also crystallizes in needles, and gives a dark cherry-red colouration with concentrated nitric acid.

Sulphoparahydroxybenzoic acid, $C_6H_3(SO_3H)(OH)CO_2H$, was prepared by Kölle by the action of sulphur trioxide on parahydroxybenzoic acid.[1] It is also obtained when the latter, or parahydroxybenzide, is heated with concentrated sulphuric acid (Klepl), and forms deliquescent needles, which are insoluble in ether. Its solution is coloured blood-red by ferric chloride; on fusion with potash, it yields protocatechuic acid.

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[1] Pelzer, *Ann. Chem. Pharm.* cxlvi. 288.

[2] *Ber. Deutsch. Chem. Ges.* v. 856.

[3] Salkowski, *Ann. Chem. Pharm.* clxiii. 36.

Acid potassium sulphoparahydroxybenzoate, $C_7H_5SO_6K + H_2O$, is a very characteristic salt, since it is even less soluble in water than acid potassium tartrate. It crystallizes from a hot solution in quadratic tablets or prisms, and from a less concentrated solution in rectangular plates which are obliquely striated (Klepl).

Parahydroxybenzoyl sulphuric acid, $C_6H_4(SO_4H)CO_2H$, occurs as an alkali salt in the urine of the dog after administration of parahydroxybenzoic acid. The potassium salt, $C_6H_4(SO_4K)CO_2K$, is obtained by heating an alkaline solution of parahydroxybenzoic acid with potassium disulphate, and crystallizes in lustrous plates or tablets, which decompose at 250° with formation of potassium sulphate and anhydrides of parahydroxybenzoic acid.[2]

SUBSTITUTION PRODUCTS OF ANISIC ACID.

2187 *Chloranisic acid*, $C_6H_3Cl(OCH_3)CO_2H$, is formed by the action of chlorine on fused anisic acid, and crystallizes from dilute alcohol in needles or rhombic prisms, which melt at 176° and volatilize without decomposition.[3]

Dichloranisic acid, $C_6H_2Cl_2(OCH_3)CO_2H$, is obtained, together with chloranil, by heating anisic acid with hydrochloric acid and potassium chlorate; it crystallizes from alcohol in large needles melting at 196°.[4]

Bromanisic acid, $C_6H_3Br(OCH_3)CO_2H$, is formed by the action of bromine on anisic acid (Cahours), the latter being kept covered with hot water.[5] It crystallizes from alcohol in needles which melt at 213°—214° and sublime in small plates.

Dibromanisic acid, $C_6H_2Br_2(OCH_3)CO_2H$. Reinecke prepared this substance by heating anisic acid to 120° with bromine and water; it crystallizes in long needles melting at 207°. On further treatment with bromine, tribromanisol and tetrabromoquinone are formed, while fuming nitric acid converts it into dibromonitro-anisol, $C_6H_2Br_2(NO_2)OH$, (3 : 5 : 4 : 1), which was previously obtained by Körner in a different manner, the constitution of the acid being thus shown.[1] When its sodium salt is distilled with lime, the methyl ether is formed, together with the basic sodium salt of dibromoparahydroxybenzoic acid :[2]

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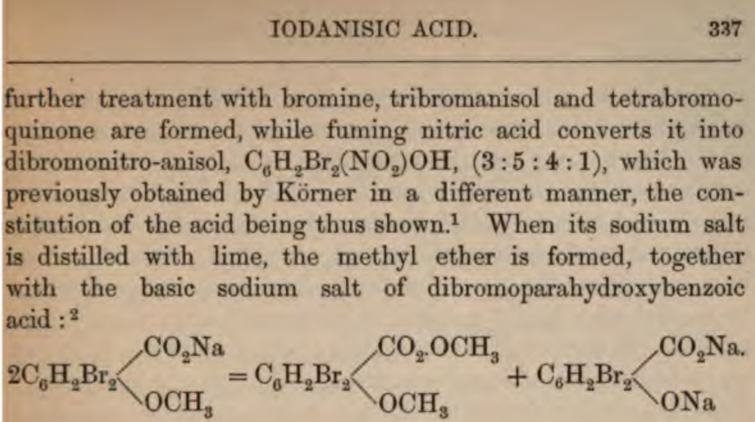
[1] *Ann. Chem. Pharm.* clxiv. 150.

[2] Baumann, *Ber. Deutsch. Chem. Ges.* xi. 1916.

[3] Cahours, *Ann. Chem. Pharm.* lvi. 312.

[4] Reinecke, *Zeitschr. Chem.* 1866, 366.

[5] Salkowski, *Ber. Deutsch. Chem. Ges.* vii. 1013.



$$2C_6H_2Br_2\Big\langle\begin{matrix}CO_2Na\\OCH_3\end{matrix} = C_6H_2Br_2\Big\langle\begin{matrix}CO_2.OCH_3\\OCH_3\end{matrix} + C_6H_2Br_2\Big\langle\begin{matrix}CO_2Na.\\ONa\end{matrix}$$

This ether crystallizes from alcohol in lustrous needles melting at 91·5°—92°.

The dibromoparahydroxybenzoic acid is also obtained by heating dibromanisic acid with hydriodic acid.[3]

Iodanisic acid, $C_6H_3I(OCH_3)CO_2H$, was prepared by Griess from diazo-amido-anisic acid,[4] while Peltzer obtained it by heating anisic acid to 145°—150° with iodine and iodic acid.[5] It crystallizes from alcohol in needles, which melt at 234·5°, and sublime in small plates.

Nitro-anisic acid, $C_6H_3(NO_2)(OCH_3)CO_2H$, was obtained by Cahours as a product of the action of nitric acid on anisic acid and anisol.[6] In order to prepare it, anisol is allowed to drop into ten times its weight of warm nitric acid, of specific gravity 1·4, the mixture boiled for a short time, and the acid then precipitated by water; it is well washed and finally freed from an admixed oil by solution in ammonia and reprecipitation by hydrochloric acid.[7] Nitro-anisic acid is slightly soluble in water, and crystallizes from alcohol in compact prisms melting at 189°. On heating with water to 220°, it decomposes into ortho-nitrophenol, methyl alcohol and carbon dioxide,[8] while aqueous ammonia at 140°—170° converts it into δ-nitro-amidobenzoic acid.[9]

Its salts have been investigated by Engelhardt.[10]

Dinitro-anisic acid, $C_6H_2(NO_2)_2(OCH_3)CO_2H$. Salkowski and Rudolph prepared this substance by dissolving anisic acid in portions of 40 grammes at a time in a well-cooled mixture of sulphuric and nitric acids, 160 grammes of the former and 140 of the latter being required for each portion of anisic acid; notwithstanding the low temperature, carbon dioxide is evolved and di- and tri-nitro-anisol are formed. The dinitro-anisic acid separates from the acid solution on standing, and is then dissolved in a cold, dilute solution of sodium bicarbonate, re-precipitated by alcohol and finally purified by re-crystallization from dilute alcohol. It forms yellowish needles melting at 181°—182°, and on boiling with caustic soda decomposes into methyl alcohol and dinitroparahydroxybenzoic acid, while it is immediately converted into chrysanisic acid by boiling, concentrated ammonia (p. 258).

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[1] Balbiano, *Gaz. Chim. Ital.* xiv. 9.

[2] *Ibid.* xiii. 65.

[3] Alessi, *ibid.* xv. 242.

[4] *Ann. Chem. Pharm.* cxvii. 54.

[5] *Ibid.* cxlvi. 302.

[6] Cahours, *ibid.* xli. 71.

[7] Salkowski, *ibid.* clxiii. 6.

[8] Salkowski and Rudolph, *Ber. Deutsch. Chem. Ges* x. 1254.

[9] Salkowski, *Ann. Chem. Pharm.* clxxiii. 35.

[10] Zinin, *ibid.* xcii. 327 ; Cahours, *ibid.* cix. 21.

Amido-anisic acid, $C_6H_3(NH_2)(OCH_3)CO_2H$, is obtained by reducing nitro-anisic acid with alcoholic ammonium sulphide.[1]

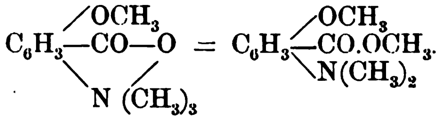
It is slightly soluble in water, readily in alcohol, and crystallizes in long, thin, four-sided prisms, which melt at 180° and are decomposed into carbon dioxide and anisidine when heated with caustic baryta (Part III. p. 249).

Methyl amido-anisate, $C_6H_3(NH_2)(OCH_3)CO_2.CH_3$, was prepared by Cahours from the methyl ether of nitro-anisic acid by reduction; it crystallizes in prisms which readily dissolve in alcohol.

Methylamido-anisic acid, $C_6H_3(NH.CH_3)(OCH_3)CO_2H$. Griess obtained this substance by heating potassium amido-anisate with methyl iodide. It is slightly soluble in hot water and cold alcohol, but more readily in hot alcohol, and melts above 200°.[2]

Trimethylamido-anisic acid, or *Trimethylanise-betaïne*, $C_{11}H_{15}NO_3 + 5H_2O$, is formed by the action of methyl iodide and caustic potash on anisic acid, and crystallizes from water in well-formed, vitreous prisms, which have a bitter taste and are neutral to litmus paper.

It is completely converted by distillation into the metameric methyl ether of dimethylamido-anisic acid:



$$C_6H_3\begin{cases}OCH_3\\ CO—O\\ N(CH_3)_3\end{cases} = C_6H_3\begin{cases}OCH_3\\ CO.OCH_3.\\ N(CH_3)_2\end{cases}$$

The latter substance is a yellowish liquid, which has a faint aromatic odour and boils at 288°.[3]

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[1] Zinin, *Ann. Chem. Pharm.* xcii. 327; Cahours, *ibid.* cix. 21.

[2] *Ber. Deutsch. Chem. Ges.* v. 1042.

[3] Griess, *ibid.* vi. 587.

ANISENYLOXIME COMPOUNDS.

2188 These bodies, which correspond to the benzenyloxime compounds (p. 207), are prepared in an exactly similar manner, anisyl chloride being gradually added to a solution of hydroxylamine hydrochloride, which is kept faintly alkaline by the addition of dilute carbonate of soda solution. A mixture of anishydroxamic acid, di-anishydroxamic acid and anisic acid is thus obtained. Boiling water extracts from this a portion of the anisic acid and all the anishydroxamic acid, these being subsequently separated by means of their barium salts, that of the former being soluble while that of the latter is insoluble in water. The dry mixture of the two acids may also be extracted with warm absolute ether, in which anishydroxamic acid is almost insoluble. The di-anishydroxamic and anisic acids are separated by treatment with a cold solution of sodium carbonate, which dissolves the latter completely, while only a small portion of the former enters into solution. The liquid is filtered rapidly, because di-anishydroxamic acid is easily decomposed by carbonate of soda, the filtrate almost neutralized with hydrochloric acid, and then saturated with carbon dioxide, all the di-anishydroxamic acid present being thus precipitated.[1]

Anishydroxamic acid, $CH_3O.C_6H_4.C(OH)NOH$, is slightly soluble in cold, readily in hot water and alcohol, but is almost insoluble in ether; it crystallizes in small plates, melting at 156°—157°, and is coloured deep violet by ferric chloride. The acid potassium salt, $C_8H_8KNO_3+C_8H_9NO_3$, forms long, flat needles, which are tolerably soluble in cold water. Lead acetate produces a thick, white precipitate[2] of $C_2H_3O_2PbC_8H_8NO_3$.

Ethyl anishydroxamate, $CH_3O.C_6H_4.C(OH)NOC_2H_5$, is formed by the action of anisyl chloride on ethylhydroxylamine; it is insoluble in water, readily soluble in alcohol, less easily in ether, from which it crystallizes in tablets, which melt at 84° and have feeble acid properties. On heating with concentrated hydrochloric acid, it is split up into anisic acid and ethylhydroxylamine.[3]

Ethylanishydroxamic acid, $CH_3O.C_6H_4.C(OC_2H_5)NOH$, is obtained by heating the ethyl ether of anisbenzhydroxamic acid with caustic potash. It is precipitated by carbon dioxide as an oily liquid, which solidifies to a crystalline mass, melting at 32°. It is readily soluble in alcohol and ether, and decomposes on heating with hydrochloric acid into ethyl anisate and hydroxylamine.[1]

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[1] Lossen, *Ann. Chem. Pharm.* clxxv. 284.
[2] Hodges, *ibid.* clxxxii. 218.
[3] Pieper, *ibid.* ccxvii. 16.

Dianishydroxamic acid, $CH_3O.C_6H_4.C(NO.CO.C_6H_4.OCH_3)OH$, is scarcely soluble in water and ether, slightly in alcohol, and crystallizes in needles, melting at 142°—143°. It is decomposed by baryta water into anisic acid and anishydroxamic acid.

Benzanishydroxamic acid, $C_6H_5.C(NO.CO.C_6H_4.OCH_3)OH$, is formed by heating benzhydroxamic acid to 100° with anisyl chloride. It crystallizes from alcohol in needles or prisms, which melt at 131°—132°. On heating with baryta water, it decomposes into anisic acid and benzhydroxamic acid, while boiling water splits it up into carbon dioxide, anisic acid and diphenyl urea. When heated alone, it yields carbon dioxide, phenyl isocyanate, anisic acid and anisanilide, $C_6H_5.NH(CO.C_6H_4.OCH_3)$.

α-Ethylbenzanishydroxamate, or *Benzanisethylhydroxylamine*, $C_6H_5.C(NO.CO.C_6H_4.OCH_3)OC_2H_5$, is obtained by the action of ethyl iodide on silver benzanishydroxamate. It crystallizes from a mixture of ether and benzene in thick, monoclinic tablets, melting at 74° (Pieper). It is decomposed by caustic potash into anisic and α-ethylbenzhydroxamic acids, and by hydrochloric acid into anisic acid, ethyl benzoate and hydroxylamine.

β-Ethylbenzanishydroxamate is formed by the action of anisyl chloride on α- or β-ethylbenzhydroxamic acid, and separates from ether in monoclinic crystals, melting at 89°. On heating with concentrated caustic potash solution, it decomposes into anisic acid and β-ethylbenzhydroxamic acid, while on dry distillation it decomposes into benzonitril, anisic acid and aldehyde.

Anisbenzhydroxamic acid, $CH_3O.C_6H_4C(NO.CO.C_6H_5)OH$, is obtained from anishydroxamic acid and benzoyl chloride; it crystallizes in needles or prisms, which melt at 147°—148°, and decompose at a higher temperature into carbon dioxide, benzoic acid, anisol isocyanate, $CON.C_6H_4.OCH_3$, and benzoylanisidine, $NH(CO.C_6H_5)C_6H_4.OCH_3$.

Ethyl anisbenzhydroxamate, or *Anisbenzethylhydroxylamine*, $CH_3O.C_6H_4C(NO.CO.C_6H_5)OC_3H_5$, crystallizes in short, four-sided, asymmetric pyramids, melts at 79° and is decomposed by caustic potash into benzoic acid and ethylanishydroxamic acid.

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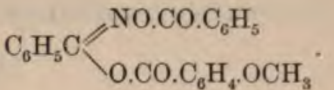
[1] Eisler, *Ann. Chem. Pharm.* clxxv. 338.

Benzethylanishydroxylamine, $C_6H_5C(NOC_2H_5)O.CO.C_6H_4.OCH_3$, is obtained by the action of anisyl chloride on the silver salt of ethylbenzhydroxamate, and separates from ether in asymmetric crystals, melting at 64°. It is decomposed by highly concentrated caustic potash into anisic acid and ethylbenzhydroxamate.

Anisethylbenzhydroxylamine, $CH_3O.C_6H_4.C(NOC_2H_5)OCO.C_6H_5$, is formed when a solution of ethylanishydroxamate in caustic potash is treated with benzoyl chloride, and forms monosymmetric crystals, melting at 93°—94°. It is split up into benzoic acid and ethyl anishydroxamate on heating with caustic potash.[1]

2189 *Hydroxylamine Derivatives containing three Acid Radicals* are formed by the action of anisyl or benzoyl chloride on the silver salts of the dihydroxamic acids. They are insoluble in water and sodium carbonate solution, and only very slightly soluble in cold alcohol. On heating with hydrochloric acid, the radical which was last introduced is split off.[2]

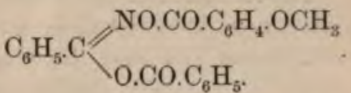
DIBENZANISHYDROXYLAMINE,



$$C_6H_5C\Big\langle\begin{matrix}NO.CO.C_6H_5\\O.CO.C_6H_4.OCH_3\end{matrix}.$$

		Melting-point.
a)	Long, monosymmetric needles or prisms .	110°—110·5°
β)	Small crystals	109°—110°

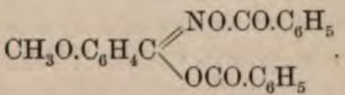
BENZANISBENZHYDROXYLAMINE,



$$C_6H_5.C\Big\langle\begin{matrix}NO.CO.C_6H_4.OCH_3\\O.CO.C_6H_5.\end{matrix}.$$

		Melting-point.
a)	Short, asymmetric prisms	113°—114°
β)	Long, rhombic prisms	124°—125°
γ)	Monosymmetric tablets; decompose on fusion	—

ANISDIBENZHYDROXYLAMINE,



$$CH_3O.C_6H_4C\Big\langle\begin{matrix}NO.CO.C_6H_5\\OCO.C_6H_5\end{matrix}.$$

		Melting-point.
a)	Lustrous monoclinic tablets	137°—137·5°
β)	Very small crystals, usually opaque . . .	109·5°—110·5°

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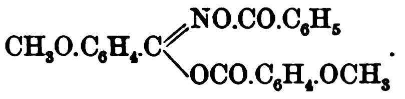
[1] Pieper, *Ann. Chem. Pharm.* ccxvii. 1.

[2] Lossen, ibid. clxxxvi. 1.

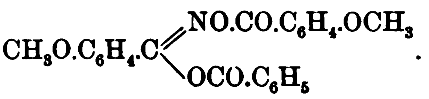
ANISBENZANISHYDROXYLAMINE,



$$\mathrm{CH_3O.C_6H_4.C}\Big\langle\begin{matrix}\mathrm{NO.CO.C_6H_5}\\ \mathrm{OCO.C_6H_4.OCH_3}\end{matrix}.$$

		Melting-point.
a)	Very small, monosymmetric tablets	152°—153°
β)	Monosymmetric tablets	148°—149°

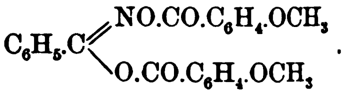
DIANISBENZHYDROXYLAMINE,



$$\mathrm{CH_3O.C_6H_4.C}\Big\langle\begin{matrix}\mathrm{NO.CO.C_6H_4.OCH_3}\\ \mathrm{OCO.C_6H_5}\end{matrix}.$$

	Melting-point.
Large, monosymmetric crystals with many faces .	147·5°

BENZDIANISHYDROXYLAMINE,



$$\mathrm{C_6H_5.C}\Big\langle\begin{matrix}\mathrm{NO.CO.C_6H_4.OCH_3}\\ \mathrm{O.CO.C_6H_4.OCH_3}\end{matrix}.$$

		Melting-point.
a)	Short, asymmetric columns	137·5°—138·5°
β)	Asymmetric tablets	137·5°—138°

Lossen remarks concerning these compounds: "The twelve substances described above afford an additional proof of the well-established fact that there are two kinds of isomerism, which must be carefully distinguished from one another. Seven isomeric substances were obtained as the products of three different methods of preparation, three being yielded by one method and two by each of the others; three further methods of preparation, different from the preceding, gave five isomeric bodies, two being formed by each method. Isomerides are, therefore, formed both by different methods and by one and the same method, but the difference between two compounds which are prepared by independent methods is not the same as that existing between the isomeric products of a single method."[1]

The latter, in fact, always give the same decomposition products on treatment with hydrochloric acid or caustic potash.

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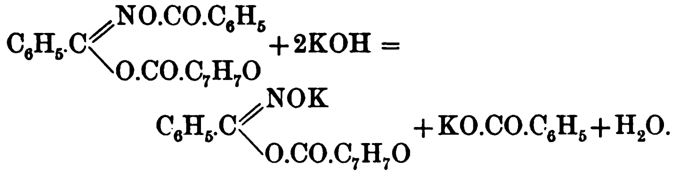
[1] *Loc. cit.* and *Ber. Deutsch. Chem. Ges.* xviii. 1189.

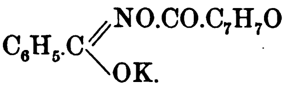
Thus benzoic acid and dianishydroxamic acid are obtained by the action of caustic potash upon the anisbenzanishydroxylamines, the same products, together with anisic acid and anisbenzhydroxamic acid, being also formed from dianisbenzhydroxylamine, while the benzdianishydroxylamines are resolved into anisic acid and benzanishydroxamic acid.

The dibenzanishydroxylamines under the same circumstances yield benzanishydroxamic acid, and not, as might have been expected, a compound metameric with this:



$$\mathrm{C_6H_5.C}\begin{cases}\mathrm{NO.CO.C_6H_5}\\ \mathrm{O.CO.C_7H_7O}\end{cases} + \mathrm{2KOH} = \mathrm{C_6H_5.C}\begin{cases}\mathrm{NOK}\\ \mathrm{O.CO.C_7H_7O}\end{cases} + \mathrm{KO.CO.C_6H_5} + \mathrm{H_2O}.$$

Lossen assumes that the decomposition first proceeds in this way, and that the compound formed changes into:



$$\mathrm{C_6H_5.C}\begin{cases}\mathrm{NO.CO.C_7H_7O}\\ \mathrm{OK}.\end{cases}$$

" A similar exchange between a metal and an acid radical has often been observed."

DIHYDROXYBENZYL AND DIHYDROXYBENZOYL COMPOUNDS.

2190 *Protocatechuicaldehyde*, or *a-Orthodihydroxybenzaldehyde*, $\mathrm{C_6H_3(OH)_2CHO.(COH : OH : OH = 1 : 3 : 4)}$, was first prepared from piperonal (p. 347) and from vanillin or its methyl ether. Tiemann and Reimer found that it is also formed by the action of chloroform on an alkaline solution of catechol.[1] In order to prepare it, a solution of 10 parts of the latter in 600 parts of 16 per cent. caustic soda solution is heated for 5—6 hours with 100 parts of chloroform in an apparatus connected with an inverted condenser, acidified with hydrochloric acid, allowed to cool, filtered from a black resinous substance and shaken out with incense.[1] This substance will be further described along with eugenol.

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[1] *Ber. Deutsch. Chem. Ges.* ix. 1269.

Properties.—Vanillin forms white needles, generally occurring in stellate aggregates, which possess a very strong taste and smell of vanilla. It melts at 80°—81°, sublimes readily, boils at 285° without decomposition when heated in an atmosphere of carbon dioxide, and dissolves in 90—100 parts of water at 14°, and in 20 parts at 75°—80°. It is scarcely soluble in cold, more readily in hot petroleum spirit. Its aqueous solution is coloured bluish violet by ferric chloride; if this solution be heated, white needles of dihydrovanillin separate out. This body, which will be described among the compounds containing two aromatic nuclei, has the following constitution:[2]

$$\begin{array}{l} C_6H_2(OH)(OCH_3)CHO \\ | \\ C_6H_2(OH)(OCH_3)CHO \end{array}.$$

Vanillin is reduced in dilute alcoholic solution by sodium amalgam to *vanillyl alcohol*, $C_6H_3(OH)(OCH_3)CH_2.OH$, which crystallizes in prisms, melting at 115°.[3]

Vanillin has an acid reaction and forms salts, which have been investigated by Carles, and by Tiemann and Haarmann; the former has also prepared bromine and iodine substitution compounds.

2191 *Isovanillin*, $C_6H_3(COH)(OH)(OCH_3)$ (1: 3: 4), is formed by heating opianic acid, $C_6H_2(COH)(OCH_3)_2CO_2H$, to 160°—170° with dilute hydrochloric acid; it crystallizes from hot water in monosymmetric prisms, which possess a vitreous lustre, and its solution is not coloured by ferric chloride; it sublimes when heated, undergoing slight decomposition;[4] its vapour has a pleasant smell, resembling that of vanilla and anise.

Methylvanillin, or *Dimethylprotocatechuicaldehyde*, $C_6H_3(OCH_3)_2$CHO, is formed by heating potassium vanillin with methyl iodide and wood-spirit.[5] Beckett and Wright prepared it by distilling opianic acid with soda lime.[6] It is slightly soluble in hot water, readily in alcohol, and crystallizes in needles, which smell like vanilla; it melts at 42°—43° and boils at 280°—285°.

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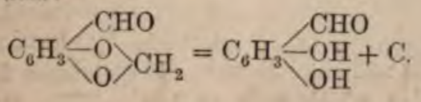
[1] Pelletier, *Ann. Chem. Pharm.* vi. 31; Sobrero, *ibid.* liv. 67.
[2] Tiemann, *Ber. Deutsch. Chem. Ges.* xviii. 3493.
[3] *Ibid.* viii. 1125; ix. 415; xviii. 1597.
[4] Wegscheider, *Monatsch. Chem.* iii. 789.
[5] Tiemann, *Ber. Deutsch. Chem. Ges.* viii. 1135
[6] *Journ. Chem. Soc.* 1876, i. 287.

vanillin, $C_6H_3(OCO.CH_3)(OCH_3)CHO$, is obtained by on of sodium vanillin on an ethereal solution of acetic de. It crystallizes in large, flat needles, melting at 77°.[1]

ovanillin, or *Vanillin glucoside*, $C_6H_3(OCH_3)(OC_6H_{11}O_5) + 2H_2O$, is formed by the oxidation of coniferin with a solution of chromic acid. It is tolerably soluble in water, eadily in alcohol, and crystallizes from dilute alcohol in needles which lose their water at 100° and melt at 192°. It adily decomposed by emulsin into grape sugar and vanillin, is converted by sodium amalgam and water into *glucovanillyl hol*, $C_6H_3(OCH_3)(OC_6H_{11}O_5)CH_2.OH + H_2O$, which crystizes in white needles, melting at 120°. When its aqueous ution is treated with a little emulsin and allowed to stand for ur or five days at 30°—40°, vanillyl alcohol is formed, and can ost easily be obtained pure by this method.[2]

Piperonal, or *Methyleneprotocatechuicaldehyde*, $C_6H_3(O_2CH_2)CHO$, was prepared by Fittig and Mielk by the oxidation of piperic acid, $C_6H_3(O_2CH_2)C_4H_4.CO_2H$, with potassium permanganate.[3] It is slightly soluble in cold, more readily in hot water and forms long, thin, lustrous plates, which have a very pleasant smell, resembling that of the heliotrope;[4] it is on this account employed in perfumery.[5]

Piperonal melts at 37°, boils at 263° and forms a vapour which has a specific gravity of 5·18.[6] A very characteristic reaction of this substance is that it decomposes into protocatechuicaldehyde and finely divided carbon when it is heated to 200° with dilute hydrochloric acid:[7]



$$C_6H_3\begin{cases}CHO\\ O\\ O\end{cases}\!\!>CH_2 = C_6H_3\begin{cases}CHO\\ OH\\ OH\end{cases} + C.$$

Oxidizing agents convert it into piperonylic acid, while sodium amalgam reduces it in boiling aqueous solution to *piperonyl*

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[1] Tiemann and Nagai, *Ber. Deutsch. Chem. Ges.* xi. 647.

[2] Tiemann, *ibid.* xviii. 1595.

[3] *Ann. Chem. Pharm.* clii. 35.

[4] This same smell is possessed by "vanillon," a kind of vanilla, which forms thick, fleshy capsules, and is obtained from the West Indies. It is only employed in perfumery for the preparation of essence of heliotrope; it contains no piperonal, but vanillin and an oil which is probably benzaldehyde. The perfumers in preparing essence of heliotrope add a little of this oil to the extract of vanillon. If a little be added to a solution of pure vanillin, both substances can be recognized by their smell for some time, but after standing for months, the mixture acquires the smell of heliotrope (Tiemann and Haarmann, *Ber. Deutsch. Chem. Ges.* ix. 1287.)

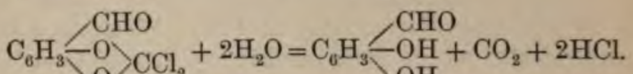
[5] *Chem. Zeit.* 1884, 173.

[6] Knecht, *Ber. Deutsch. Chem. Ges.* x. 1274.

[7] Fittig and Remsen, *Ann. Chem. Pharm.* clxviii. 97.

alcohol, $C_6H_3(O_2CH_2)CH_2.OH$, which is slightly soluble in cold, more readily in hot water, and forms long, colourless crystals, melting at 51°.[1]

Dichloropiperonal, $C_6H_3(O_2CCl_2)COH$. When one molecule of piperonal is heated with three molecules of phosphorus pentachloride, the compound $C_6H_3(O_2CCl_2)CHCl_2$ is formed. It is an oily liquid, which is decomposed by water into hydrochloric acid and dichloropiperonal; the latter crystallizes from toluene in needles, which melt at 90° and undergo the following decomposition when heated with water:



$$C_6H_3\begin{cases}CHO\\ O\\ O\end{cases}\!\!>CCl_2 + 2H_2O = C_6H_3\begin{cases}CHO\\ OH\\ OH\end{cases} + CO_2 + 2HCl.$$

Protocatechuicaldehyde was first prepared according to this method by Fittig and Remsen.

2192 *β Methylorthodihydroxybenzaldehyde*, or *β-Metamethoxysalicylaldehyde*, $C_6H_3(OH)(OCH_3)CHO$ ($CHO : OH : OCH_3 = 1 : 2 : 3$), is formed together with vanillin by heating guaiacol with caustic soda and chloroform. On distillation with steam it passes over first as a liquid, which smells like salicylaldehyde, boils at 264°—265° in a current of carbon dioxide, stains the skin yellow and forms a deep yellow solution in alkalis. Ferric chloride added to an alcoholic solution produces a green colouration containing a shade of violet.[2]

Metadihydroxybenzaldehyde, or *β-Resorcylaldehyde*, $C_6H_3(OH)_2CHO$ ($CHO : HO : HO = 1 : 2 : 4$), is obtained, along with resorcyldialdehyde, $C_6H_2(OH)_2(CHO)_2$, by heating resorcinol with caustic soda and chloroform.[3] It crystallizes from water in yellowish needles, which melt at 134°—135°; its solution is coloured reddish brown by ferric chloride. It is an unstable substance and gradually decomposes in moist air into a red powder.

Orthomethoxyparahydroxybenzaldehyde, $C_6H_3(OH)(OCH_3)CHO$ ($CHO : OCH_3 : OH = 1 : 2 : 4$), is formed, together with the following compound and two resorcyldialdehydes, by heating methylresorcinol with caustic soda and chloroform.[4] It is readily soluble in alcohol, slightly in water and benzene, and crystallizes from the latter in lustrous plates melting at 153°. Its aqueous solution is coloured a faint violet by ferric chloride. The acetyl-derivative, $C_6H_3(OC_2H_3O)(OCH_3)CHO$, is formed by adding the potassium compound to an ethereal solution of acetic anhydride; it crystallizes in needles, melting at 86°.

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[1] Fittig and Remsen, *Ann. Chem. Pharm.* clix. 138.

[2] Tiemann and Koppe, *Ber. Deutsch. Chem. Ges.* xiv. 2020.

[3] Tiemann and Lewy, *ibid.* x. 2212.

[4] Tiemann and Parrisius, *ibid.* xiii. 2365.

Paramethoxysalicylaldehyde, ($COH : OH : OCH_3 = 1 : 2 : 4$), may also be obtained by heating γ-resorcyldialdehyde with caustic potash and methyl iodide. It is almost insoluble in water and crystallizes in plates, which have a characteristic, pleasant, aromatic odour, melt at 62°—63° and are very readily volatile. It forms an intensely yellow solution in alkalis; ferric chloride produces a deep reddish yellow colouration in an alcoholic solution.

	Melting-point.
Dimethyl-β-resorcylaldehyde, needles	68°—69°.
Diethyl-β-resorcylaldehyde, lustrous plates	71°—72°.

Paradihydroxybenzaldehyde, or *Gentisinaldehyde*, ($CHO : OH : OH = 1 : 2 : 5$), has been prepared from quinol by the action of chloroform and caustic soda. It is readily soluble in water and alcohol, and crystallizes in flat, lustrous yellow needles, melting at 99°; its aqueous solution is coloured a transient bluish green by ferric chloride and intensely yellow by alkalis.[1]

Methylparadihydroxybenzaldehyde, or *Metamethoxysalicylaldehyde*, ($CHO : OH : OCH_3 = 1 : 3 : 5$), has been obtained from methylquinol.[2] It is a yellow oil which has an aromatic odour, solidifies in a freezing mixture to a radiating mass and then melts at 4°; it boils at 247°—248° in a current of carbon dioxide. It stains the skin yellow, forms an intensely yellow solution in alkalis and in alcoholic solution is coloured a permanent bluish green by ferric chloride. Its acetyl-compound crystallizes in needles, melting at 63°.

	Melting-point.
Dimethylparadihydroxybenzaldehyde, fine needles	51°
Ethylparadihydroxybenzaldehyde, thick, yellow prisms	51·5°
Diethylparadihydroxybenzaldehyde, small needles[3]	60°

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[1] Tiemann and Müller, *Ber. Deutsch. Chem. Ges.* xiv. 1986.

[2] *Ibid.* 1990.

[3] Hantzsch, *Journ. Prakt. Chem.* [2] xxii. 464.

DIHYDROXYBENZOIC ACIDS. $C_6H_3\begin{cases}OH\\CO.OH\\OH\end{cases}$

[illegible] designate the positions of the [illegible]

[illegible] DIHYDROXYBENZOIC ACID [illegible]

[illegible] on an [illegible] carbohydro- [illegible] hydroquinone [illegible] Two years later Strecker found [illegible] acid with potash, which [illegible] first thought that [illegible] less carbon in [illegible] It decom- [illegible] should [illegible] properties [illegible] most [illegible] had been [illegible] products of carbo- [illegible] decisively [illegible] observed by [illegible]

[illegible] from various carbon [illegible] protocatechuic [illegible] first [illegible] many resins [illegible] paracresol- [illegible]

[illegible]

[illegible] xxxix. [illegible]

sulphonic acid,[1] bromanisic acid, iodoparahydroxybenzoic acid, sulphoparahydroxybenzoic acid and sulphometahydroxybenzoic acid,[2] is of theoretical interest.

It is best prepared from East Indian kino, which is obtained by making incisions in the bark of *Pterocarpus Marsupium* ; the sap flows out and dries to a dark red, transparent mass, which is employed in medicine as an adhesive, and for many purposes as a substitute for catechu. One part of the finely-powered kino is then gradually brought into a well-stirred melt of three parts of caustic soda kept at a low temperature. When the mass has become coloured a light orange brown, it is dissolved in 20 parts of water, and the solution acidified with sulphuric acid, and allowed to stand for twenty-four hours. The filtrate is extracted with ether, the latter evaporated and the residue repeatedly crystallized from water.[3] The aqueous solution of the acid may also be precipitated with lead acetate, the precipitate washed and finally decomposed by sulphuretted hydrogen (Barth and Hlasiwetz).

According to Eijkman, protocatechuic acid occurs in the fruit of *Illicium religiosum*.[4]

It crystallizes in monoclinic needles, containing one molecule of water which is lost at 100°, and melts at 194°;[5] it dissolves in 53—55 parts of water at 14° and in 3·5—3·7 parts at 75°—80°,[6] is very soluble in alcohol, less so in ether, and almost insoluble in boiling benzene. Its aqueous solution is coloured an intense bluish green by ferric chloride, the colour being changed to dark red by the addition of sodium carbonate. The solutions of its salts are coloured violet by ferrous sulphate. It reduces an ammoniacal silver solution, but not Fehling's solution; on dry distillation, or when heated to 330°—350° with caustic soda, it decomposes into carbon dioxide and catechol. When nitrogen trioxide is passed into its ethereal solution, oxalic and dihydroxytartaric acids are formed (Part III. p. 58), together with smaller quantities of dinitrophenol, picric acid, dinitrodihydroxyquinone and nitroparahydroxybenzoic acid.[7]

Protocatechuic acid is produced along with benzoic acid when gum benzoin is fused with caustic potash; a compound of the

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[1] Barth, *Ann. Chem. Pharm.* cliv. 364.
[2] *Ibid.* clix. 232.
[3] Stenhouse, *ibid.* clxxvii. 188.
[4] *Ber. Deutsch. Chem. Ges.* xviii. Ref. 281.
[5] Barth and Schmidt, *ibid.* xii. 1265.
[6] Tiemann and Nagai, *ibid.* x. 211.
[7] Gruber, *ibid.* xii. 514.

by the action of potassium permanganate on coniferin, and crystallizes from hot water in fine prisms, which lose their water of crystallization at 100°, and melt at 210°—212°. It is decomposed by emulsin or by boiling with dilute acids into grape sugar and vanillic acid.[1]

Acetylvanillic acid, $C_6H_3(OCH_3)(OCO.CH_3)CO_2H$, is formed by heating vanillic acid with acetic anhydride,[2] and from eugenol acetate, $C_6H_3(OCH_3)(OC_2H_3O)C_3H_5$, acetylferulic acid,[3] $C_6H_3(OCH_3)(OC_2H_3O)C_2H_2.CO_2H$, acetylcreosol,[4] $C_6H_3(OCH_3)(OC_2H_3O)CH_3$ and acetylhomovanillic acid[5] by oxidation with potassium permanganate. It crystallizes from dilute alcohol in fine needles, which melt at 142°, and are decomposed on boiling with caustic potash into acetic and vanillic acids.

Benzoylvanillic acid, $C_6H_3(OCH_3)(OCO.C_6H_5)CO_2H$, is prepared by the oxidation of benzoyleugenol, and crystallizes from dilute alcohol in small plates which have a peculiar surface lustre, and melt at 178°.[6]

Isovanillic acid, $C_6H_3(OH)(OCH_3)CO_2H$, ($CO_2H : OH : OCH_3 = 1 : 3 : 4$). Tiemann found that when dimethylprotocatechuic acid is heated with dilute hydrochloric acid, vanillic acid and an isomeric methylprotocatechuic acid are formed,[7] the latter being, as was proved by Beckett and Wright,[8] identical with an acid which Matthiessen and Foster had previously obtained by heating hemipinic acid, $C_6H_2(OCH_3)_2(CO_2H)_2$, with hydrochloric acid.[9] According to Matsmoto, who proposed the name isovanillic acid, it is most readily prepared by heating 2 parts of dimethylprotocatechuic acid to 160°—170° with a mixture of 25 parts of hydrochloric acid of specific gravity 1·2 and 50 parts of water for four to five hours. The product is repeatedly crystallized from water in order to remove vanillic and protocatechuic acids which are formed in the reaction, and is then freed from any unaltered dimethylprotocatechuic acid by conversion into the acetyl compound, which is then recrystallized and saponified by dilute caustic potash.[10]

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[1] Tiemann and Reimer, *Ber. Deutsch. Chem. Ges.* viii. 515.
[2] Tiemann and Nagai, *ibid.* viii. 1142.
[3] Tiemann, *ibid.* ix. 409.
[4] Tiemann and Mendelsohn, *ibid.* x. 57.
[5] Tiemann and Nagai, *ibid.* x. 201.
[6] Kraaz and Tiemann, *ibid.* xv. 2068.
[7] *Ibid.* viii. 513.
[8] *Journ. Chem. Soc.* 1876, i. 302.
[9] *Proc. Roy. Soc.* xii. 502.
[10] *Ber. Deutsch. Chem. Ges.* xi. 125.

Isovanillic acid crystallizes in lustrous, transparent prisms, melting at 250°, which dissolve in 1.700 parts of water at 14°, and in 160 parts at 100°. It is readily soluble in alcohol and ether; it gives no colour reaction with ferric chloride.

Acetylisovanillic acid, $C_6H_3(OCO.CH_3)(OCH_3)CO_2H$, crystallizes from dilute alcohol in scales, melting at 206°—207°.

2195 *Veratric acid* or *Dimethylprotocatechuic acid*, $C_6H_3(OCH_3)_2CO_2H$. In the year 1839, E. Merck discovered veratric acid, $C_9H_{10}O_4$,[1] in the seeds of *Veratrum Sabadilla*, and W. Merck then observed that it decomposes into carbon dioxide and veratrol, $C_8H_{10}O_2$, on heating with caustic baryta.[2] By the oxidation of methyleugenol, Grabe and Borgmann obtained dimethoxybenzoic acid,[3] which was shown by Tiemann[4] and by Erlenmeyer and Wassermann[5] to be identical with the dimethylprotocatechuic acid which Kölle had prepared by heating protocatechuic acid with caustic potash, methyl iodide and wood-spirit;[6] Körner then showed that this compound is also identical with veratric acid, veratrol being dimethylcatechol.[7] Veratric acid is also formed when veratrin and pseudoaconitine are heated with alcoholic potash.[8] In order to prepare it, 1 part of methyleugenol, $C_6H_3(OCH_3)_2C_3H_5$, is shaken up with 10—15 parts of water, and a solution of 3·5 parts of potassium permanganate in 20—30 parts of water heated to 80—90° gradually added. The filtrate is concentrated by evaporation and precipitated with hydrochloric acid.[9] Veratric acid dissolves in 2.100 parts of water at 14°, and in 160 parts at 100°, and crystallizes from a concentrated solution at a temperature above 50° in anhydrous needles, while crystals containing a molecule of water are obtained from very dilute solutions at any temperature below this. It melts at 174°—175° and can be sublimed. It dissolves readily in alcohol and ether; ferric chloride produces no colouration.

Methyl veratrate, $C_6H_3(OCH_3)_2CO_2.CH_3$, is formed, together with methyl protocatechuate and methyl isovanillate, when protocatechuic acid is heated with caustic potash, methyl iodide and wood spirit,[10] no methyl vanillate being formed.[11]

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[1] *Ann. Chem. Pharm.* xxix. 188.

[2] *Ibid.* cviii. 60.

[3] *Ibid.* clviii. 282.

[4] *Ber. Deutsch. Chem. Ges.* viii. 514.

[5] *Ann. Chem. Pharm.* clxxix. 366.

[6] *Ibid.* clix. 240.

[7] *Ber. Deutsch. Chem. Ges.* ix. 582.

[8] Wright and Luff, *Journ. Chem. Soc.* 1878, i. 160 and 352.

[9] Tiemann and Matsmoto, *Ber. Deutsch. Chem. Ges.* ix. 937.

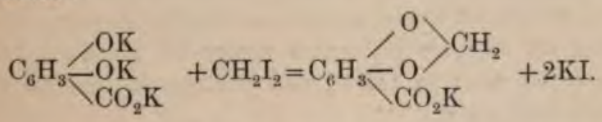
[10] Matsmoto, *ibid.* xi. 122.

[11] Tiemann, *Ber. Deutsch. Chem. Ges.* viii. 513.

The ether is obtained pure when a solution of the acid in anhydrous methyl alcohol is saturated with hydrochloric acid, or when vanillic acid is heated with caustic potash and methyl iodide. It crystallizes in odourless needles, melts at 59°—60° and boils at about 300° (Matsmoto).

	Melting-point.	Boiling-point.
Ethyl veratrate,[1] $C_6H_3(OCH_3)_2CO_2.C_2H_5$	43°—44°	295°—296°
Ethylvanillic acid,[2] $C_6H_3(OC_2H_5)(OCH_3)CO_2H$ . . .	193°—194°	—
Diethylprotocatechuic acid,[3] $C_6H_3(OC_2H_5)_2CO_2H$, ...	149°	—

Piperonic acid, $C_6H_3(O_2CH_2)CO_2H$, was prepared by Fittig and Mielk by the oxidation of piperic acid or piperonal with potassium permanganate,[4] while Fittig and Remsen obtained it by heating protocatechuic acid with caustic potash and methylene iodide:[5]



$$C_6H_3\begin{cases}OK\\OK\\CO_2K\end{cases} + CH_2I_2 = C_6H_3\begin{cases}O\\O\end{cases}\!\!>CH_2 \ \ (CO_2K) + 2KI.$$

It occurs in small quantity in Paracoto bark, which is collected on the river Mapiri in Bolivia, and has been detected in true Coto bark, which is also found in Bolivia.[6]

Piperonic acid is scarcely soluble in cold water, slightly in boiling water, from which it separates in small needles, or, on very gradual cooling, in characteristic crystals, which resemble in appearance small twisted threads of sewing cotton. It is also slightly soluble in ether and cold alcohol, separating from a hot alcoholic solution in larger crystals. It is obtained in the purest state by sublimation, which yields large, compact, glittering prisms with acute terminal planes; it melts at 227·5°—228·5°, but sublimes at a lower temperature.

When it is heated with phosphorus pentachloride, a liquid chloride is formed which yields a chlorinated acid on decomposition with cold water; this substance is probably a dichloropiperonic acid and is resolved on heating with water into

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[1] Tiemann and Matsmoto, *Ber. Deutsch. Chem. Ges.* ix. 942.

[2] Tiemann, *ibid.* viii. 1130; Wassermann, *Ann. Chem. Pharm.* clxxix. 379.

[3] Kölle, *ibid.* clix. 245.

[4] Kölle, *ibid.* clii. 40.

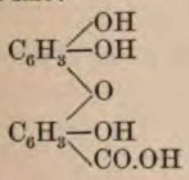
[5] *Ibid.* clxviii. 93.

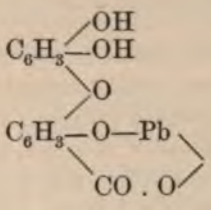
[6] Hesse and Jobst, ibid. cxcix. 63.

salt. It is ground up with dilute hydrochloric acid pressed, and repeatedly crystallized from hot water. In order to remove any adhering colouring matter, it is dissolved in water and treated with lead acetate. A current of sulphuretted hydrogen is then passed through the hot liquid, which is subsequently filtered and allowed to cool; the pure maclurin is thus obtained as a light yellow, crystalline powder. It becomes anhydrous at 130°, and melts at 200°. On boiling with water and barium carbonate one molecule of carbon dioxide is evolved for every two molecules of maclurin present (Benedikt), while the salt $C_{13}H_8PbO_6 + H_2O$ is deposited in yellow plates when lead acetate is added to the boiling solution (Hlasiwetz and Pfaundler).

When maclurin is boiled with concentrated caustic potash solution or heated to 120° with dilute sulphuric acid, it decomposes smoothly into protocatechuic acid and phloroglucinol.

Benedikt therefore proposes the following formulæ for maclurin and its lead salt:[1]





Luteolin, $C_{20}H_{14}O_8$, was discovered by Chevreul in weld (*Reseda lutea*),[2] and analyzed by Moldenhauer,[3] who obtained numbers which led to the formula given above, while Paraf and Schützenberger calculated the composition $2C_{12}H_8O_5+3H_2O$ from the results of their investigation and somewhat unsatisfactory analyses.[4] It is obtained by extracting the dried plant with water containing 5—6 per cent. of alcohol, concentrating the filtrate by evaporation and purifying the crude luteolin thus obtained by recrystallization from alcohol or a mixture of water and glycerol.

It crystallizes in small, yellow needles, which dissolve in 14,000 parts of cold water, in 5,000 parts at 100° and in 37 parts of alcohol. It readily forms a deep yellow solution in alkalis, and dissolves in cold sulphuric acid forming a reddish yellow solution from which it is precipitated by water. A small quantity of ferric chloride produces a green colouration, which passes into brownish red on the addition of more of the reagent.

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[1] *Ann. Chem. Pharm.* clxxx. 114.

[2] Berzelius, *Jahresb.* xi. 280.

[3] *Ann. Chem. Pharm.* c. 180.

[4] *Compt. Rend.* lii. 92.

Its hot aqueous solution dyes wool, mordanted with alum, a beautiful daffodil-yellow (Chevreul). On fusion with potash it is decomposed with evolution of hydrogen into phloroglucinol and protocatechuic acid :[1]

$$C_{20}H_{14}O_8 + 3H_2O = 2C_7H_6O_4 + C_6H_6O_3 + H_2.$$

Rochleder states, however, that the amount of phloroglucinol formed is much greater than corresponds to this equation. The formula of luteolin is by no means accurately determined and its constitution is quite unknown.

SYMMETRIC METADIHYDROXYBENZOIC ACID OR α-RESORCYLIC ACID (1 : 3 : 5).

2197 This substance is obtained by fusing β-disulphobenzoic acid,[2] metabromosulphobenzoic acid and parabromosulphobenzoic acid[3] with caustic potash. It crystallizes with one and a half molecules of water in needles or prisms, which melt at 232°—233°, are tolerably soluble in cold, readily in hot water, alcohol and ether, and give no colouration with ferric chloride. On fusion with caustic soda it decomposes above 300° into resorcinol and carbon dioxide.[4] A very characteristic reaction is that when heated with 4 parts of sulphuric acid to 140°, a deep red solution is formed from which water precipitates green flocks of anthrachrysone, $C_{14}H_4(OH)_4O_2$, which is a derivative of anthracene, and is also formed by the dry distillation of the acid. Lead acetate does not produce a precipitate when added to an aqueous solution of the acid.

Ethyl α-resorcylate, $C_6H_3(OH)_2CO_2.C_2H_5$, crystallizes from water in long prisms which melt below 100°.

Dimethyl-α-resorcylic acid, $C_6H_3(OCH_3)_2CO_2H$, is formed when α-resorcylic acid is heated with caustic potash, methyl iodide and wood-spirit, and when dimethylorcinol is oxidized with potassium permanganate.[1] It crystallizes from hot water in fine needles, which melt at 175°—176°.

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[1] Rochleder, *Journ. Prakt. Chem.* xcix. 433.
[2] Barth and Senhofer, *Ann. Chem. Pharm.* clix. 217.
[3] Böttinger, *Ber. Deutsch. Chem. Ges.* viii. 374.
[4] Barth and Schreder, *ibid.* xii. 1258.

Diethyl-α-resorcylic acid, $C_6H_3(OC_2H_5)_2CO_2H$, was prepared by Barth and Senhofer from the acid by the action of ethyl iodide.[2] It forms elongated prisms, which melt at 87°—88°, and are decomposed by distillation with lime into carbon dioxide and diethylresorcinol.[3]

α-Bromoresorcylic acid, $C_6H_2Br(OH)_2CO_2H$, is formed by the action of bromine water on an aqueous solution of α-resorcylic acid, and crystallizes from hot water in long needles, which melt at 253°, and give a yellowish brown colouration with ferric chloride. It gives the same reaction with sulphuric acid as α-resorcylic acid, and is converted into gallic acid by fusion with caustic potash (Barth and Senhofer).

ASYMMETRIC METADIHYDROXYBENZOIC ACID OR β-RESORCYLIC ACID, (1:2:4).

2198 This acid is formed when paracresolsulphonic acid,[4] and α-disulphobenzoic acid[5] are fused with caustic potash, and may also be obtained, together with a large amount of resorcinol, when its aldehyde is fused for a short time with caustic potash.[6] It may also be prepared, together with γ-resorcylic acid and dihydroxyphthalic acid, $C_6H_2(OH)_2(CO_2H)_2$, by heating 1 part of resorcinol with 4 parts of ammonium carbonate and 5 parts of water to 120°—130°,[7] and still more readily by heating resorcinol in an open flask with a concentrated solution of potassium bicarbonate. It is very slightly soluble in cold water, and crystallizes from a hot solution in needles containing one and a half molecules of water, one of which is lost on exposure to the air (Fahlberg). It melts at 204°—206°, and simultaneously decomposes into carbon dioxide and resorcinol. Its solution is coloured dark red by ferric chloride, and does not give a precipitate with lead acetate.

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[1] Tiemann and Streng, *Ber. Deutsch. Chem. Ges.* xiv. 2002.

[2] *Ann. Chem. Pharm.* clxiv. 121.

[3] Barth, *Ber. Deutsch. Chem. Ges.* xi. 1569.

[4] Ascher, *Ann. Chem. Pharm.* clxiv. 11.

[5] Blomstrand, *Ber. Deutsch. Chem. Ges.* v. 1088 ; Fahlberg, *Amer. Chem. Journ.* ii. 196.

[6] Tiemann and Reimer, *Ber. Deutsch. Chem. Ges.* xii. 997 ; Tiemann and Parrisius, *ibid.* xiii. 2358.

[7] Brunner and Senhofer, *ibid.* xiii. 2356 ; *Ber. Wien. Akad.* 1879, ii. 504.

Orthomethyl-β-resorcylic acid, $C_6H_3(OH)(OCH_3)CO_2H$ ($OCH_3 : OH = 2 : 4$), is formed when the acetyl-derivative of its aldehyde is oxidized with potassium permanganate and the product decomposed by caustic potash. It is tolerably soluble in water, does not crystallize well, and gives no colouration with ferric chloride.[1]

Paramethyl-β-resorcylic acid ($OH : OCH_3 = 2 : 4$). The methyl ether is prepared by adding sodium to a solution of β-resorcylic acid in wood-spirit and then heating with methyl iodide, the acid being obtained from this by boiling with caustic potash (Tiemann and Parrisius); it is also formed when sodium methylresorcinol is heated to 215° in a current of carbon dioxide:[2]

$$C_6H_4(OCH_3)ONa + CO_2 = C_6H_3(OCH_3)(OH)CO_2Na.$$

It crystallizes from hot water in lustrous needles, which melt at 15[illegible]° and decompose into methylresorcinol and carbon dioxide when rapidly heated. Its aqueous solution is coloured an intense reddish violet by ferric chloride.

Dimethyl-β-resorcylic acid, $C_6H_3(OCH_3)_2CO_2H$, is not readily formed by the further methylation of the preceding compound, but may be obtained by the oxidation of its aldehyde with potassium permanganate; it crystallizes from hot water in fine needles, melting at 108° (Tiemann and Parrisius).

Diethyl-β-resorcylic acid, $C_6H_3(OC_2H_5)_2CO_2H$, was prepared in a similar manner; it forms needles which melt at 99°.[3]

ADJACENT METADIHYDROXYBENZOIC ACID OR γ-RESORCYLIC ACID (1:2:6).

2199 The formation of this acid has already been mentioned; it is very soluble in water, and crystallizes in fine, fascicular needles, which contain one molecule of water and commence to fuse at 140°, a partial decomposition into resorcinol and carbon dioxide occurring, which becomes complete at a higher temperature. Its aqueous solution is coloured a deep bluish violet by ferric chloride.

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[1] Tiemann and Parrisius, *Ber. Deutsch. Chem. Ges.* xiii. 2375.

[2] Körner and Bertoni, *ibid.* xiv. 847.

[3] Tiemann and Lewy, *ibid.* x. 2215.

γ-Bromoresorcylic acid, $C_6H_2Br(OH)_2CO_2H + H_2O$, is formed by the action of bromine on an ethereal solution of the acid. It is slightly soluble in cold water, readily in alcohol, and crystallizes in fine prisms, which lose their water at 100° and melt at 184° with decomposition. It is coloured violet by ferric chloride.

Dimethyl-γ-resorcylic acid, $C_6H_3(OCH_3)_2CO_2H$. When metadinitrobenzene is treated with methyl alcohol and potassium cyanide, *methoxynitrobenzonitril*, $C_6H_3(NO_2)(OCH_3)CN$, is formed; it crystallizes from chloroform in pliant needles, which melt at 171°, and are converted on heating with methyl alcohol and caustic potash into *dimethoxybenzonitril*, $C_6H_3(OCH_3)_2CN$, which crystallizes from alcohol in needles or rectangular tablets, melting at 118°. It boils at about 310°, and when heated with baryta water yields dimethyl-γ-resorcylic acid, which forms crystals melting at 179°, and is converted into γ-resorcylic acid by heating with caustic potash.

If methoxynitrobenzonitril is heated with caustic potash and ethyl alcohol, *ethoxymethoxybenzonitril*, $C_6H_3(OCH_3)(OC_2H_5)CN$, is formed, and crystallizes from alcohol in prisms or tablets, melting at 66°. This compound is also formed when metadinitrobenzene is treated with ethyl alcohol and potassium cyanide, and the *ethoxynitrobenzonitril*, $C_6H_3(NO_2)(OC_2H_5)CN$, thus formed, which melts at 137°, is heated with methyl alcohol and caustic potash. A new and simple proof is thus afforded of the identity of the positions 1 and 6 in the benzene nucleus.[1]

HYDROXYSALICYLIC ACID OR PARADIHYDROXYBENZOIC ACID (1 : 2 : 5).

2200 This isomeride has been prepared by fusing iodosalicylic acid with caustic potash;[2] it is more readily obtained, however, by fusing bromosalicylic acid with caustic soda,[3] and is also

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[1] Lobry de Bruyn, *Ber. Deutsch. Chem. Ges.* xviii. Ref. 148; *Chem. Centralbl.* 1884, 119; 1885, 357.

[2] Lautemann, *Ann. Chem. Pharm.* cxx. 311; Liechti, *ibid.* Suppl. vii. 144; Demole, *Ber. Deutsch. Chem. Ges.* vii. 1438; Goldberg, *Journ. Prakt. Chem.* [2] xix. 371.

[3] Leppert and Rakowski, *Ber. Deutsch. Chem. Ges.* viii. 788.

[illegible] acid or m-aminosalicylic acid.[1] [illegible] with potassium bicarbonate, water [illegible] Hlasiwetz and Habermann, by [illegible] with caustic [illegible] acid, which they named [illegible] that it was different from [illegible] subsequently found. However, [illegible] acid.[3] It is readily [illegible] crystallizes in needles or [illegible] and gives a deep blue colouration [illegible] Fehling's solution and [illegible] on heating. On dry distillation it [illegible]

[illegible] crystallizes from [illegible] which have a pleasant fruity odour and [illegible]

[illegible] acid, [illegible] CO_2H [illegible] was prepared by [illegible] and Bertoni [illegible] methylquinol [illegible] acid. [illegible] the acetyl- [illegible] potassium per- [illegible] soda.[6] It [illegible] at 142°, and [illegible] with ferric chloride.

[illegible] CO_2H, is formed [illegible] crystallizes from hot water [illegible]

[illegible] are compared, it [illegible] its aldehyde, and also [illegible] the hydroxyls in the ortho-position, give a [illegible] colouration with ferric chloride. Those compounds, on the other hand, in which a hydroxyl is situated in the ortho position with regard to a carboxyl, and which can therefore be considered as derivatives of salicylic acid, give a blue to dark red colouration, while those in which the hydroxyls are in the meta position, give as little colouration as meta-hydroxybenzoic acid.

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[1] Goldberg, *loc. cit.*

[2] Senhofer and Sarlay, *Monatsh. Chem.* ii. 448.

[3] *Ann. Chem. Pharm.* clxxv. 66.

[4] *Ibid.* clxxx. 343.

[5] *Ber. Deutsch. Chem. Ges.* xiv. 848.

[6] *Ibid.* xiv. 1097.

[7] *Ibid.* 1293.

According to theory, six dihydroxybenzoic acids can exist. In addition to the five just mentioned, two others have been shortly described. One of these was obtained by Leeds by allowing toluene saturated with nitrogen peroxide to stand in a loosely covered vessel for a whole summer. It crystallizes from alcohol in small plates, which sublime at 170° without fusing and give no colouration with ferric chloride.[1]

Aescioxalic acid, $C_7H_6O_4$, is the name given by Rochleder to a compound which he obtained, together with formic acid, oxalic acid and frequently protocatechuic acid, by boiling aesculetin, $C_9H_6O_4$, with concentrated caustic potash or baryta water. It forms an extremely fine crystalline mass and gives a reddish brown colouration with ferric chloride, which is changed by sodium carbonate to purple-violet, while ferrous sulphate and a little carbonate of soda produce an intense blue colouration.[2]

TRIHYDROXYBENZOIC ACIDS, $C_6H_2(OH)_3CO_2H$.

GALLIC ACID.

2201 The history of this substance goes hand in hand with that of tannic acid. In the introduction to organic chemistry it has already been mentioned how Pliny states that paper dipped in an extract of nut-galls was used to ascertain whether verdigris was adulterated with green vitriol. He also informs us that the juice of nut-galls was used to recognize a kind of *alumen*, employed for dyeing wool black, which was either natural green vitriol or a mineral containing this salt.

It was also known in very early times that certain parts of plants, which have an astringent taste, give a black colouration with bodies containing iron. In addition to nut-galls, Paracelsus enumerates the sap of oaks, alders, &c., which colour solutions of iron and copper black, and Libavius used this reaction in the analysis of mineral waters, which were coloured black in the presence of iron, but only darkened when containing copper; he thus discovered the presence of copper vitriol in the "Weinbrunnen" at Schwalbach.

Tachenius states in *Hippocrates chymicus*, 1766, that tincture of nut-galls produces various coloured precipitates with solutions of iron, copper, lead and mercury, and separates metallic gold from solutions of its salts. Other astringent plants have a similar action, which he compares with that of the volatile alkalis, since these remove acids from vitriols in a similar manner. Lemery takes the same view in his paper on the kinds of vitriol and the formation of ink, which is published in the *Memoirs of the Paris Academy* for 1707; nut-galls, according to him, are of an absorbent or alkaline nature, and therefore act like salt of tartar, lime-water, ammonia, &c. That the latter do not produce a black precipitate with iron is accounted for by the fact that the sulphurous particles present in nut-galls are absent in the alkalis. As a proof of this he mentions that when these absorbent substances are made to combine with sulphur, they do give a black precipitate with solutions containing iron.

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[1] *Ber. Deutsch. Chem. Ges.* xiv. 482.

[2] *Jahresb. Chem.* 1867, 752.

Bergman, on the other hand, suggested in 1775, that a vegetable acid is contained in astringent substances, and in his *Elemens de Chymie* 1777, published by Morveau, Maret, and Durande, it is stated that on the dry distillation of nut-galls a substance sublimes which blackens solutions of iron and behaves as a true acid. In order to obtain it in a purer condition, Retzius, in 1783, treated the dried extract of nut-galls with cold water, and in this way obtained a substance which had the properties of an acid and effervesced with alkaline carbonates. In 1786, Scheele prepared gallic acid by exposing extract of nut-galls to the air in a warm place and frequently removing the film of mould which was formed. The crystalline precipitate which gradually separated out was purified by recrystallization. He observed that when gallic acid is heated a body sublimes which also precipitates iron salts, but which he considered to be different from gallic acid, a view which was also taken by Berthollet in his *Statique chimique*, 1803, while Fourcroy and Berzelius believed that the sublimate is the pure gallic acid, this being denied by Braconnot and also by Pelouze (Part III., p. 181). The astringent constituent of nut-galls, subsequently called tannic acid, was first recognized as a distinct substance by Deyeux in 1793, and more definitely by Seguin in 1795, after which Berzelius obtained it in a pure or almost pure condition. It had already been noticed that it is readily converted into gallic acid, but the relations of the two substances had not been explained, although many chemists had investigated the question.

Pelouze and Berzelius gave to tannic acid the formula $C_{18}H_{18}O_{12}$, which was altered by Liebig to $C_{18}H_{16}O_{12}$, since the latter explains in a simple manner its conversion into gallic acid in presence of water and oxygen: "From one atom of tannic acid and four atoms of oxygen, exactly two atoms of gallic acid and two atoms of carbonic acid are formed, while according to the formula $C_{18}H_{18}O_{12}$, two atoms of hydrogen remain over, and no one knows what becomes of them."[1] At a later period he proposed the formula $C_{18}H_{10}O_9 + 3aq$, which can be expressed as the sum of the formulæ of anhydrous acetic acid and gallic acid; he had found that tannic acid can be converted into gallic acid without the intervention of oxygen by simply boiling for a few minutes with caustic potash, or better, dilute sulphuric acid.[2] He could not, however, detect any acetic acid and suggested that an isomeride of this is formed, which, however, from the behaviour of tannic acid towards sulphuric acid, could not be a sugar[3] as had been suggested by Stas.[4]

Wetherill, on the other hand, assumed that tannic and gallic acids were isomeric,[5] while Mulder gave to the former the formula $C_{14}H_{10}O_9$, according to which it forms two molecules of gallic acid by the assumption of the elements of water;[6] subsequently, however, he altered his formula to $C_{14}H_{12}O_9$, and looked upon gallic acid as an oxidation product.[7]

Tannic acid was then carefully investigated in Liebig's laboratory by Strecker, who succeeded in resolving it into grape sugar and gallic acid, expressing the reaction by the following equation:[8]

$$C_{27}H_{22}O_{17} + 4H_2O = 3C_7H_6O_5 + C_6H_{12}O_6.$$

This view was almost universally accepted, the more so as other tannic matters had proved to be glucosides, and as the formation of gallic acid by fermentation received a simple explanation. According to Strecker's equation, 29·1 per cent. of grape sugar should be formed, while he only obtained 15—22 per cent., and Rochleder found that by proper purification the amount can be reduced to 4 per cent. without altering the chemical and physical properties of the tannic acid to any important extent.[1] His results confirmed those of Knop, who succeeded in converting 95 per cent. of the tannic acid into gallic acid, ellagic acid, $C_{14}H_6O_8$, and a carbohydrate being also formed.[2] Stenhouse had previously arrived at similar results, having found that by the use of sufficiently dilute sulphuric or hydrochloric acid almost the whole of the tannic acid can be converted into gallic acid.[3]

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[1] *Ann. Chem. Pharm.* x. 172.

[2] *Ibid.* xxvi. 128.

[3] *Handb. Chem.* 854.

[4] *Ann. Chem. Pharm.* xxx. 205.

[5] *Journ. Prakt. Chem.* xlii. 247.

[6] *Jahresb. Chem.* 1848, 524.

[7] *Ibid.* 1858, 261.

[8] *Ann. Chem. Pharm.* xc. 328.

Rochleder then assumed that the sugar is formed from some admixture, and that tannic acid stands in the same relation to gallic acid as dextrin to grape sugar. Hlasiwetz remarks on this question: "If tannin is not a glucoside, it may perhaps be a digallic acid, which corresponds to gallic acid in the same way as diethylene alcohol to ordinary glycol, and it would then have the formula which was first proposed for it by Mulder:

$$2C_7H_6O_5 - H_2O = C_{14}H_{10}O_9.$$

"The analyses of tannin and its salts agree with this composition as well as can be expected in the case of a substance which is so difficult to purify." [4]

Löwe, however, came to a different conclusion; he found that silver nitrate and arsenic acid are reduced by gallic acid with formation of ellagic acid and a substance which has all the properties of tannic acid, so that he considered the latter to be an oxidation product of gallic acid.[5] He subsequently found that the correct formula of tannic acid is $C_{14}H_{10}O_9$, but assumed that gallic acid is not formed from it only by assumption of water, but that a molecular change takes place.[6]

Schiff, on the contrary, showed conclusively that arsenic acid and also phosphorus oxychloride simply exert a dehydrating action, and that the digallic acid thus formed is identical with tannic acid. This question will be more fully considered under the latter.

2202 Gallic acid occurs ready formed in nut-galls, sumach and divi-divi, the fruit of *Caesalpinia coriaria*.[7] It is also found in the leaves of the red bear-berry (*Arctostaphylos Uva ursi*),[8] in China tea,[9] and in red Bündner wine.[10] Etti obtained it by heating kinoïn, $C_{14}H_{12}O_6$, with hydrochloric acid;[1] it is also formed when di-iodoparahydroxybenzoic acid,[2] bromoprotocatechuic acid,[3] bromoveratric acid,[4] and α-bromoresorcylic acid,[5] are fused with caustic potash. According to Lautemann it is also formed in this way from di-iodosalicylic acid,[6] but Demole failed to obtain it by this method,[7] and it is probable that Lautemann's compound, which was only obtained in small quantity, is the isomeric pyrogallolcarboxylic acid.

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[1] *Chem. Centralbl.* 1858, 579.

[2] *Pharm. Centralbl.* 1855, 658.

[3] *Chem. Soc. Mem.* i. p. 147.

[4] *Ann. Chem. Pharm.* cxliii. 295.

[5] *Journ. Prakt. Chem.* cii. 111; ciii. 446.

[6] *Fresenius' Zeitschr.* xi. 365.

[7] Stenhouse, *Chem. Soc. Mem.* i. 137.

[8] Kawalier, *Jahresb. Chem.* 1852, 683.

[9] Hlasiwetz and Malin, *Zeitschr. Chem.* 1867, 271.

[10] Simler, *Jahresb. Chem.* 1861, 923.

In order to prepare gallic acid, Scheele's method, which is stated by Liebig to give the best yield, is made use of. Finely powdered nut-galls are extracted with cold water and the solution allowed to stand in a warm place, the precipitated acid being recrystallized from boiling water.

According to Braconnot, the entire nut-galls may be moistened with water in summer or allowed to stand in a warm place until they form a paste, which is then extracted with boiling water.[8]

The spores of *Penicillium glaucum* or *Aspergillus niger* are necessary to set up fermentation.[9] Wittstein recommends the addition of beer yeast; he thus obtained almost 50 per cent. from Chinese nut-galls, while without the yeast the yield only amounted to 17 per cent.[10] One hundred pounds of Turkish nut-galls, treated by Scheele's method, give 24 pounds of gallic acid.[11]

It crystallizes in silky needles or asymmetric prisms, containing one molecule of water, which is lost at 120°, has an acid, astringent taste, and dissolves in 130 parts of water at 12·5°, and in 3 parts at 100°. It is more readily soluble in alcohol, since 27·95 parts dissolve in 100 parts of absolute alcohol at 15°, and 18·90 parts in 100 parts of 90 per cent. alcohol, while 100 parts of ether only dissolve 2·5 parts.[12]

Gallic acid commences to melt above 220° and decomposes into carbon dioxide and pyrogallol when more strongly heated. It is readily oxidized, reduces Fehling's solution and the salts of the noble metals, and in alkaline solution absorbs oxygen. When it is added to ferric chloride, a partial reduction ensues and a black-blue precipitate is formed, which dissolves in the excess of ferric chloride with a green colour. According to Etti, the colouration depends mainly on the concentration of the solutions, and varies between black-blue, black-green, blue, greenish and brownish green. An excess of gallic acid destroys the colour and effects complete reduction to ferrous chloride; a solution of pure ferrous sulphate in absence of air is therefore not altered by it, but on exposure to air is coloured a bright blue, and deposits a black precipitate without becoming decolourized.

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[1] *Ber. Deutsch. Chem. Ges.* xi. 1881.
[2] Barth and Senhofer, *ibid.* viii. 1884.
[3] *Ibid.*
[4] Matmoso, *ibid.* xi. 140.
[5] Barth and Senhofer, *Ann. Chem. Pharm.* clxiv. 118.
[6] *Ibid.* cxx. 137.
[7] *Ber. Deutsch. Chem. Ges.* vii. 1441.
[8] *Ann. Chim. Phys.* ix. 181.
[9] Tieghem, *Zeitschr. Chem.* 1868, 222.
[10] *Vierteljahrsschr. Pharm.* ii. 72.
[11] Steer, *Jahresber. Chem.* 1856, 482.
[12] Bourgoin, *Bull. Soc. Chim.* xxix. 245.

Gallic acid in alcoholic or alkaline solution reduces paranitrobenzyl chloride to paranitrotoluene. Digallic acid and pyrogallol have a similar action.[1]

It is converted by the action of potassium chlorate and hydrochloric acid into tricarballylic acid, $C_3H_5(CO_2H)_3$, and *isotrichlorglyceric acid*, $CCl_3.C(OH)_2.CO_2H$, which crystallizes in needles and is readily decomposed by alkalis into chloroform and oxalic acid.[2]

When gallic acid is heated with sulphuric acid, rufigallic acid or hexhydroxyanthraquinone, $C_{14}H_2O_2(OH)_6$, is formed, while an acid solution of potassium permanganate produces hydrorufigallic acid, $C_{14}H_2O_5$.

Gallic acid is not precipitated by gelatine solution, and can thus be distinguished from tannic acid and other similar substances.

2203 *The Gallates* have been chiefly investigated by Büchner.

Sodium gallate, $C_6H_2(OH)_3CO_2Na + 3H_2O$, is obtained by adding alcoholic soda to a solution of the acid in alcohol as a granular, crystalline precipitate, which crystallizes from a very concentrated aqueous solution in pointed yellow plates.

Potassium gallate, $C_6H_2(OH)_3CO_2K + C_6H_2(OH)_3CO_2H + H_2O$, is a light, crystalline powder which is prepared in a similar manner to the sodium salt; the normal salt has not yet been obtained.

Ammonium gallate, $C_6H_2(OH)_3CO_2NH_4 + H_2O$, is formed when ammonia is passed into a solution of the acid in absolute alcohol, and crystallizes from water in fine needles. When its solution is boiled, the acid salt, $C_6H_2(OH)_3CO_2NH_4 + C_6H_2(OH)_3CO_2H$, is deposited on cooling in splendid crystals.[3] It is also formed when dry gallic acid is saturated with ammonia, the excess of the latter allowed to evaporate in a vacuum and the residue crystallized from water; it contains water of crystallization (Robiquet).

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[1] Pellizzari, *Gazz. Chem. Ital.* xiv. 481.

[2] Schreder, *Ann. Chem. Pharm.* clxxvii. 282; see also Claisen and Antweiler, *Ber. Deutsch. Chem. Ges.* xiii. 1938.

[3] Etti, *Ber. Deutsch. Chem. Ges.* xvii. 1821.

Calcium gallate, $(C_7H_5O_5)_2Ca + 3H_2O$, forms thin, crystalline crusts, consisting of needles. When lime-water is added to a solution of the acid a dirty green precipitate is produced.

Barium gallate, $(C_7H_5O_5)_2Ba + 3H_2O$, is obtained by neutralizing a boiling solution of the acid with barium carbonate; it crystallizes in small plates, which do not readily redissolve in water. If the freshly-prepared solution be treated with baryta-water, a precipitate of $C_7H_2O_5Ba_2 + 5H_2O$ is formed, which rapidly becomes coloured dark blue on exposure to the air in the moist state (Hlasiwetz).

Lead gallate. Lead acetate added to a hot solution of an excess of the acid produces a precipitate of $2C_7H_4O_5Pb + H_2O$, which soon changes to a lustrous, crystalline powder. If, however, an excess of the lead acetate be employed, a flocculent precipitate is formed, which becomes yellow and crystalline on boiling and has the formula $C_7H_2O_5Pb_2$ (Liebig).

Iron gallate. A splendid blue precipitate is obtained when the acid is added to a mixture of three molecules of a ferrous salt with two molecules of a ferric salt.[1]

Ethyl gallate, $2C_6H_2(OH)_3CO_2.C_2H_5 + 5H_2O$, is formed when hydrochloric acid is passed into the alcoholic solution of the acid. It is slightly soluble in cold, readily in hot water and alcohol, and crystallizes in pointed prisms, which lose their water at 100°.[2] It is slightly soluble in chloroform, from which it separates in anhydrous crystals.[3] It behaves towards ferric chloride, silver nitrate, &c., in the same manner as the free acid, and on heating decomposes into alcohol and pyrogallol, accompanied, however, by other products.[4] When acid sodium carbonate is added to its aqueous solution, small crystals of $C_6H_2(OH)_3CO_2.C_2H_5 + C_6H_2(OH)_2(ONa)CO_2.C_2H_5$, are formed, which are scarcely soluble in cold water (Ernst and Zwenger). Lead acetate added to an aqueous solution of the ether produces a finely divided precipitate of $(C_6H_2(CO_2.C_2H_5)O_3)_2Pb_3$ (Schiff).

Triethylgallic acid, $C_6H_2(OC_2H_5)_3CO_2H$. The ethyl ether of this substance is obtained by heating ethyl gallate with caustic

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[1] Barreswill, *Compt. Rend.* xvii. 739.
[2] Grimaux, *Bull. Soc. Chim.* ii. 94.
[3] Ernst and Zwenger, *Ann. Chem. Pharm.* clix. 28.
[4] Schiff, *ibid.* clxiii. 209.

In order to avoid oxidation, ammonium sulphite must be added to the solution or the operation must be conducted in an atmosphere free from oxygen.[1] It crystallizes from hot water in large, colourless plates and decomposes on boiling with hydrochloric acid into gallic acid and ammonia.

2204 *Digallic acid, Tannic acid* or *Tannin*, $C_6H_2(OH)_3CO.OC_6H_2(OH)_2CO_2H$. The name of tannic acids has been applied to a whole series of substances, which are weak acids, have an astringent taste, give black-blue or dark green compounds with salts of iron, and combine with animal skins to form leather, for which purpose they are largely employed. These bodies do not stand in any intimate chemical relation to each other, and the tannic acid derived from nut-galls, the constitution of which is known, is alone referred to here.

The nut-galls in which it occurs are of two kinds: the ordinary, Turkish or Levant variety, which are produced by the puncture of the gall-fly (*Cynips Gallae tinctoriae*) in the young shoots of *Quercus lusitanica, var. infectoria* and probably some other species, and the Chinese or Japanese nut-galls, which are formed by a plant-louse (*Aphis chinensis*) on the leaf-stalks and young twigs of *Rhus semialata*. In addition to these modes of occurrence, tannic acid has hitherto only been observed in sumach, the leaves and twigs of *Rhus coriaria*.[2]

Stenhouse, who found that tannic acid from sumach is converted into gallic acid by dilute sulphuric acid, says: "Sumach, therefore, appears to approach the nature of nut-galls more closely than any of the other astringent substances. This fact is well known to Turkey-red dyers, who have long successfully employed sumach as a substitute for galls."

In order to prepare tannin, the method of Pelouze was formerly employed, according to which the nut-galls are extracted with ordinary ether, containing both alcohol and water. The solution thus obtained separates into two layers, the upper of which consists of water and ether containing gallic acid and a little tannin, while the syrupy lower layer is a solution of tannin in water and ether and is evaporated to dryness.

A mixture of 12 parts of ether and 3 parts of alcohol is now used for the extraction, 12 parts of water being added to the extract and the alcohol and ether removed by distillation. The

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[1] Knop, *Jahresber. Chem.* 1854, 431; Schiff and Pons, *Ber. Deutsch. Chem. Ges.* xv. 2591; xviii. 487; Etti, *ibid.* xvii. 1820.

[2] Stenhouse, *Chem. Soc. Mem.* i. 137; Löwe, *Fres. Zeitschr.* xii. 128.

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

[illegible] is heated [illegible] is [illegible]

[illegible]

which gives all the reactions of tannin, is also in favour of this formula:[1]

$$C_6H_2(OH)_3CO.OK + BrC_6H_2(OH)_2CO.OH =$$
$$C_6H_2(OH)_3CO.O.C_6H_2(OH)_2CO.OH + KBr.$$

Properties.—Tannin is a colourless, amorphous mass, which is left on the evaporation of its solution in brittle, vitreous masses, which become coloured yellow in the light, even when exposed in closed vessels. It reddens litmus and has a very strong astringent taste, is readily soluble in water, less so in absolute alcohol, and almost insoluble in absolute ether. Finely-powdered tannin coagulates in ether which contains water, and then deliquesces, so that it can be employed to detect the presence of water in ether. If water be slowly dropped into the vessel containing the thick solution covered by ether, a point is attained at which three layers are formed.[2] This occurs when 100 ccms. of water and 150 ccms. of ether are present to 100 grms. of tannin; the lowest layer contains most tannic acid, the middle layer some tannic acid and a large amount of water while the upper layer consists almost entirely of ether, but contains a little tannic acid.[3]

Tannin is insoluble in carbon disulphide, chloroform, petroleum ether, benzene, &c. Its aqueous solution gives a black-blue colouration and precipitate with ferric salts, a partial reduction taking place (Wackenroder); ferrous sulphate produces in a concentrated solution a white, gelatinous precipitate which becomes coloured blue in the air.

When tannin is heated it darkens at 150°—160°, and at 215° decomposes into water, carbon dioxide and pyrogallol, which volatilize, while metagallic acid or melangallic acid is left behind; this substance alone is formed when tannic acid is rapidly heated to 250°, and is a black, amorphous, tasteless mass. Tannin very readily undergoes oxidation; strongly ozonized air produces complete combustion, oxalic acid being formed as an intermediate product (Schönbein); it reduces the salts of copper, silver, mercury, gold, &c. In alkaline solution it rapidly absorbs oxygen, the liquid becoming coloured dark. Tannin is precipitated from aqueous solution by dilute hydrochloric acid, sulphuric acid, common salt, potassium chloride, potassium acetate and other salts, but not by nitric acid or sodium sulphate. Animal skin removes it from solution completely; it precipitates gelatine solution, egg albumen, alkaloids and other substances.

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[1] Hunt, *Chem. News*, lii. 49.

[2] Bolley, *Ann. Chem. Pharm.* cxv. 63.

[3] Luboldt, *Jahresb. Chem.* 1859, 296.

The Tannates. Tannin decomposes carbonates and is a monobasic acid, the salts of which are amorphous and difficult to prepare pure. Many of them are insoluble precipitates, such as the tannates of lead, copper, tin, and antimony, and these may be used for the quantitative estimation of the acid.

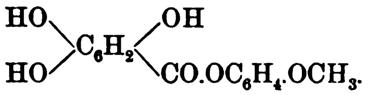
Tannin, or rather the material containing it, is employed in medicine, dyeing, the manufacture of inks, the clarification of beer and wine, &c. It is not adapted for use as a tanning agent.

Penta-acetyltannin, $C_{14}H_5(C_2H_3O)_5O_9$, is obtained by boiling tannin with acetic anhydride for one hour; it is insoluble in water and separates from boiling alcohol in white spherical or warty aggregates of crystals, which melt at 137°. Its solution is precipitated by lead acetate, but is not coloured by ferric chloride (Schiff).

Kinoïn, $C_{14}H_{12}O_6$, was discovered by Etti in Malabar kino, the dried sap of *Pterocarpus Marsupium* (p. 351). It crystallizes in prisms, which are slightly soluble in cold, readily in hot water and alcohol; its solution is coloured red by ferric chloride. On heating to 120° with hydrochloric acid, it decomposes into methyl chloride, catechol and gallic acid:

$$C_{14}H_{12}O_6 + H_2O + HCl = CH_3Cl + C_6H_6O_2 + C_7H_6O_5.$$

It is therefore gallylcatechol methyl ether, and probably has the following constitution:



Kino-red, $C_{28}H_{22}O_{11}$, is an astringent substance which also occurs in kino, and is formed by heating kinoïn to 120°—130°. It is a red, resinous substance, which is slightly soluble in water, readily in alcohol and alkalis, gives a dirty-green colouration with ferric chloride, and precipitates gelatine solution. On heating to 160°—170°, it melts with loss of water and is converted into an amorphous red compound, $C_{28}H_{20}O_{10}$, which may also be obtained by heating kino-red with dilute hydrochloric or sulphuric acids. On dry distillation, the larger portion becomes carbonized, phenol, catechol and a small amount of anisol or guaiacol being formed.[1]

2205 *Sinapin*, $C_{16}H_{23}NO_5$. Henry and Garot discovered in the seeds of the white mustard, a crystalline compound, containing both sulphur and nitrogen, to which they gave the name of sulphosinapin,[2] and which was subsequently recognized by Babo and Hirschbrunn as sinapin thiocyanate.[3] Robiquet and Boutron Charlard, repeating the research of Henry and Garot, obtained another substance,[4] which Will and Laubenheimer named sinalbin, and which is resolved into acid sinapin sulphate, sinalbin mustard oil, and grape sugar, by the action of myrosin in aqueous solution (Vol. III., Part II., p. 393).

Sinapin, which is generally classed among the alkaloids, is extremely deliquescent, but forms stable salts.

Sinapin thiocyanate, $C_{16}H_{23}NO_5.HSCN$, is obtained from the powdered seeds by first extracting them with ether and cold alcohol, and then boiling up with 90 per cent. alcohol. A very voluminous crystalline mass, which bears a strong resemblance to quinine sulphate, separates out on cooling. It crystallizes from a dilute, hot, aqueous solution in large, fascicular groups of needles, which melt at 176°,[5] and are only slightly soluble in cold alcohol and water.

Acid sinapin sulphate, $C_{16}H_{23}NO_5,H_2SO_4 + 2H_2O$, is obtained by adding sulphuric acid to a concentrated, hot solution of the thiocyanate; it crystallizes in rectangular plates, has an acid reaction and is readily soluble in water.

The normal sulphate may be prepared from the acid by neutralizing with baryta water and evaporating the filtrate; it forms an extremely soluble crystalline mass. The nitrate and hydrochloride of sinapin can be prepared from it by means of barium nitrate or chloride, and crystallizes in fine, very soluble needles. The hydrochloride combines with mercuric chloride to form the compound $C_{16}H_{23}NO_5,HCl + HgCl_2$, which crystallizes from water in thin, lustrous prisms (Will and Laubenheimer).

When the sulphuric acid is completely removed by baryta water from a solution of the sulphate, a solution of free sinapin is obtained which has a deep yellow colour, is alkaline to litmus, and precipitates the salts of the heavy metals. It decomposes on evaporation, the colour changing through green and red into brown, and a non-crystalline residue being left.

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[1] *Ber. Deutsch. Chem. Ges.* xi. 1879.

[2] Berzelius, *Jahresber.* vi. 242 ; xii. 263.

[3] *Ann. Chem. Pharm.* lxxxiv. 10.

[4] *Ibid.* xii. 266.

[5] Remsen and Coale, *Amer. Chem. Journ.* vi. 50.

If sinapin thiocyanate be boiled with baryta water or caustic potash solution, it decomposes into thiocyanic acid, sinapic acid and a base, which was named sinkalin by Babo and Hirschbrunn, but has since been identified as choline (Vol. III., Part II., p. [illegible]).

$$C_{16}H_{23}NO_5.CNSH + 2H_2O = CNSH + C_{11}H_{12}O_5 + C_5H_{15}NO_2$$

Sinapic acid, $C_{11}H_{12}O_5$, is best prepared according to Remsen and Coale by boiling sinapin with baryta water and decomposing the precipitate which is formed with hydrochloric acid. It is only slightly soluble in cold water and alcohol and crystallizes from a hot solution in small, yellowish, transparent prisms, melting at 192°. Its alkaline solution rapidly turns green, red, and brown in the air. The addition of alcohol to the freshly prepared solution of the potassium salt precipitates it in iridescent plates which rapidly change after the removal of the alcohol. Calcium chloride and barium chloride produce white precipitates, and ferric chloride gives a rose-red or fine purple-red precipitate, a partial reduction being also effected. Lead salts added to a neutral solution of the acid produce a white precipitate which soon becomes green and then brown, while the colourless precipitates yielded by the salts of silver and mercury are rapidly reduced; the metal is immediately separated from gold solutions.

The barium salt alone has been obtained in a condition suitable for analysis by precipitating a solution of the acid, neutralized by potash or ammonia, with barium chloride, or more readily by boiling the acid with baryta water in absence of air: it has the composition $C_{11}H_{10}BaO_5$.

Babo says: "Since it is a matter of some difficulty to obtain another salt of the acid in a state fitted for analysis, and I could not spare too much material for this research, the question whether the acid is mono- or dibasic must remain for the present undecided."

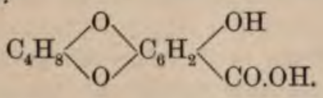
This point was settled by Remsen and Coale, who heated weighed amounts of the acid with calcium or barium carbonate and determined the amount of metal which had entered into solution; they found that sinapic acid is monobasic, and that the normal barium salt has the formula $(C_{11}H_{11}O_5)_2Ba$.

The insoluble barium salt is therefore a basic compound, corresponding to the basic salicylates, and sinapic acid should therefore be a hydroxy-acid, as is proved to be the case by the existence of the following compound.

Acetylsinapic acid, $C_{11}H_{11}(C_2H_3O)O_5$, is obtained by boiling the acid with acetic anhydride, and forms crystals, which are soluble in hot water and melt at 281°.

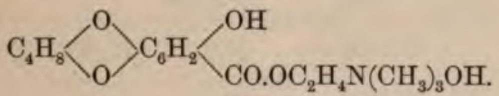
When sinapic acid is heated on platinum foil, vapours are given off which smell like incense, and are also formed when the acid is fused with caustic potash, pyrogallol being among the products.

According to Remsen and Coale, sinapic acid is probably butylenegallic acid:

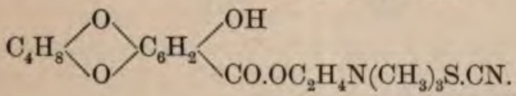


$$C_4H_8{<}\begin{matrix}O\\O\end{matrix}{>}C_6H_2{<}\begin{matrix}OH\\CO.OH.\end{matrix}$$

If this view be correct, the following formulæ will represent the constitution of sinapin and its thiocyanate:

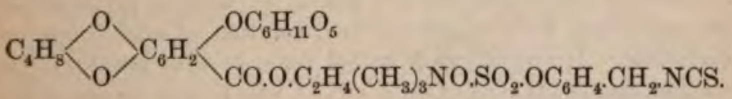


$$C_4H_8{<}\begin{matrix}O\\O\end{matrix}{>}C_6H_2{<}\begin{matrix}OH\\CO.OC_2H_4N(CH_3)_3OH.\end{matrix}$$



$$C_4H_8{<}\begin{matrix}O\\O\end{matrix}{>}C_6H_2{<}\begin{matrix}OH\\CO.OC_2H_4N(CH_3)_3S.CN.\end{matrix}$$

If it be further assumed that sinalbin contains two molecules of water of crystallization, its constitution may be represented as follows:



$$C_4H_8{<}\begin{matrix}O\\O\end{matrix}{>}C_6H_2{<}\begin{matrix}OC_6H_{11}O_5\\CO.O.C_2H_4(CH_3)_3NO.SO_2.OC_6H_4.CH_2.NCS.\end{matrix}$$

Gallocyanin. This dye, which was discovered by Köchlin, and which is also known as solid-violet (*violet solide*), is manufactured by heating nitrosodimethylaniline hydrochloride with gallic acid or tannin in alcoholic solution. It is a crystalline substance with a green metallic lustre, readily dissolves in alkalis, and yields salts which crystallize well, that with aniline forming small, green crystals. Gallocyanin forms a blue solution in concentrated sulphuric acid. It is used for dyeing cotton and in calico printing, since it forms a beautiful violet-black

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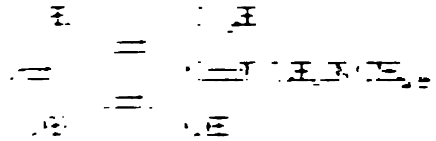

PYROGALLOLCARBOXYLIC ACID

[illegible] compound is formed together with phloroglucinol [illegible] by heating pyrogallol to 130° with [illegible] or more simply by heating pyrogallol in [illegible] with a concentrated solution of acid potassium carbonate.[3] It crystallizes from hot water in silky needles of the composition $C_6H_2(OH)_3CO_2H + H_2O$, which become anhydrous at 115° and have a markedly acid taste. One part dissolves at 12.5° in 767 parts of water; it is readily soluble in alcohol, but less so in ether. On heating in a current of hydrogen, a gradual evolution of carbon dioxide accompanied by fusion sets in at 195°–200°, while it sublimes slowly, but without decomposition, in a current of carbon dioxide. Its aqueous solution is coloured

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[1] [illegible], *Chem. News*, xlvii. 170; Pabst, *Bull. Soc. Chim.* xxxviii. 162; *Chemiker-Zeit.* [illegible] 1144.

[2] Senhofer and Brunner, *Monatsh. Chem.*, i. 468.

[3] Kostanecki, *Ber. Deutsch. Chem. Ges.* xviii. 3202.

violet by very dilute ferric chloride, while a strong solution produces a greenish brown colouration; ferrous sulphate produces no immediate colouration, but the liquid becomes violet on standing. The same colouration is produced by concentrated sulphuric acid which contains a trace of nitric acid.

Baryta water and lime water produce blue precipitates which are at first so finely divided that the liquid appears clear. The acid is coloured dark brown by strong potash solution, especially on boiling. It reduces ammoniacal silver solution in the cold and imparts a green colour to Fehling's solution, reduction taking place on warming.

It differs sharply from gallic acid in remaining unacted on by sulphuric acid at 140°, no rufigallic acid being formed; decomposition, accompanied by a violent evolution of gas, sets in, however, at a higher temperature.

The Pyrogallolcarboxylates. The following salts are characteristic:

Calcium pyrogallolcarboxylate, $(C_7H_5O_5)_2Ca + 4H_2O$, separates from a hot solution in hard, granular crystalline masses.

Barium pyrogallolcarboxylate, $(C_7H_5O_5)_2Ba + 5H_2O$, crystallizes from a hot solution in hard, yellow prisms.

Basic lead pyrogallolcarboxylate, $C_7H_2Pb_2O_5 + H_2O$, is a white, flocculent precipitate, which becomes anhydrous at 100°.

Ethyl pyrogallolcarboxylate, $2C_6H_2(OH)_3CO_2.C_2H_5 + 3H_2O$, is insoluble in cold water, but readily in alcohol and ether, and separates from a hot aqueous solution in crystals, which become anhydrous over sulphuric acid or at 100°, at which temperature they commence to sublime, and then melt at 102.° Ferric chloride colours the aqueous solution greenish brown.

Triethylpyrogallolcarboxylic acid, $C_6H_2(OC_2H_5)_3CO_2H$. The ethyl ether of this substance is prepared by heating the preceding compound with caustic potash, ethyl iodide and alcohol. It is an odourless, volatile liquid, which is readily decomposed by alcoholic potash.[1] The free acid is slightly soluble in cold, more readily in hot water and alcohol, and crystallizes in long, silky needles, melting at 100·5°. It was first obtained from triethyldaphnetic acid, $C_6H_2(OC_2H_5)_3C_2H_2.CO_2H$, by oxidation with potassium permanganate, its aldehyde $C_6H_2(OC_2H_5)_3CHO$, being simultaneously formed as an oily liquid which gradually solidifies to a crystalline mass melting at 70°.[2]

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[1] Will and Albrecht, *Ber. Deutsch. Chem. Ges.* xvii. 2100.

[2] *Ber. Deutsch. Chem. Ges.* xvii. 1087.

PHLOROGLUCINOLCARBOXYLIC ACID.

This acid is obtained by heating phloroglucinol with acid potassium carbonate and water to 130°.[1] It crystallizes in needles, which contain a molecule of water and are only slightly soluble in water, more readily in alcohol, very readily in ether and have an acid taste. The water is lost at 100°, carbon dioxide being also slowly evolved. On boiling with water it is decomposed smoothly into phloroglucinol and carbon dioxide. Its aqueous solution is coloured an intense blue by ferric chloride, which soon changes to dirty brown, and its alkaline solution turns brown in the air.

When its alcoholic solution is saturated with hydrochloric acid, carbon dioxide is evolved and phloroglucinol diethyl ether is formed (Part III. p. 187).

HYDROXYQUINOLCARBOXYLIC ACID.

The following derivatives of this acid are alone known:

Triethylhydroxyquinolcarboxylic acid, $C_6H_2(OC_2H_5)_3CO_2H$, is formed by the oxidation of the two isomeric triethylaesculetic acids $C_6H(OC_2H_5)_3C_2H_2CO_2H$, with potassium permanganate, and crystallizes from hot water in fine needles, melting at 134°. Its aldehyde, $C_6H_2(OC_2H_5)_3COH$, is also formed and crystallizes from alcohol in splendid pointed prisms, melting at 95°.

Trimethylhydroxyquinolcarboxylic acid, $C_6H_2(OCH_3)_3CO_2H$, resembles the ethyl compound and melts at 108°—109°.[2]

These compounds were at first considered as derivatives of phloroglucinolcarboxylic acid. When the triethylcompound is distilled with lime, however, a triethoxybenzene is obtained, which melts at 34°, and is therefore different from the triethyl ether of pyrogallol or phloroglucinol, so that it must be that of hydroxyquinol.[3]

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[1] *Ber. Deutsch. Chem. Ges.* xvii. 2103.

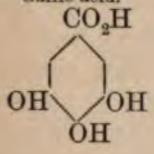
[2] Will, *ibid.* xvi. 2112.

[3] Will and Albrecht, *ibid.* xvii. 2103.

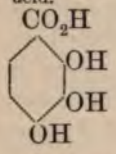
CONSTITUTION OF THE TRIHYDROXY-BENZOIC ACIDS.

According to theory, six of these compounds can exist, but only four are known:

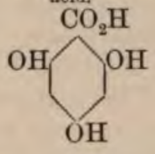
Gallic acid.



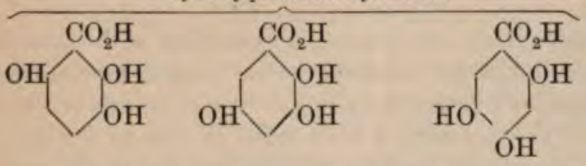
Pyrogallolcarboxylic acid.



Phloroglucinolcarboxylic acid.



Hydroxyquinolcarboxylic acids.



The constitution of gallic acid is determined by its formation from bromoprotocatechuic acid and α-bromoresorcylic acid, whence it also follows that pyrogallol is an adjacent trihydroxybenzene, and that in phloroglucinol the hydroxyls are symmetrically arranged (Part III., p. 181). The latter can only yield one carboxylic acid, so that the constitution of phloroglucinolcarboxylic acid is determined; this is confirmed by its formation from daphnetic acid, in which a hydroxyl is known to be in the ortho-position to the carboxyl.

The constitution of the hydroxyquinolcarboxylic acid from aesculetic acid has not yet been determined.

QUINIC ACID, $C_6H_7(OH)_4CO_2H$.

2207 Count Claude de la Garaye, in 1746, obtained a crystalline deposit[1] from the extract of Peruvian bark, which became known as *Sel essentiel de la Garaye.* Hermbstädt of Berlin showed in 1785 that this "Chinasalz" is a salt of lime,[2] and Hofmann, an apothecary of Leer, in 1790 detected in it a

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[1] *Chimie hydraulique*, Paris, 1746, 114.

[2] *Crell's Ann.* ii. 115.

[illegible]

When lead dioxide is added to its aqueous solution, carbon dioxide is evolved and the reaction may be carried on by heating the mixture, lead quinate and quinol being formed:[1]

$$C_7H_{12}O_6+O = C_6H_6O_2+CO_2+3H_2O.$$

When it is heated with manganese dioxide and sulphuric acid, quinone is formed, while protocatechuic acid may be obtained by evaporating a solution of the acid to which bromine has been added,[2] or by fusing the acid with caustic potash,[3] or caustic soda,[4] as well as, together with a large amount of benzoic acid, by heating quinic acid to 150° with fuming hydrochloric acid.[5]

Fuming hydriodic acid reduces it at 120° to benzoic acid:[6]

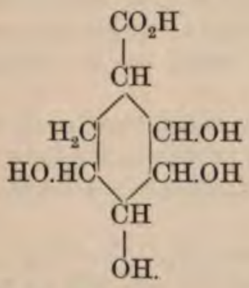
$$C_7H_{12}O_6+2HI = C_7H_6O_2+4H_2O+I_2.$$

On heating with concentrated hydrochloric acid to 140°—150°, parahydroxybenzoic acid and quinol are formed; it dissolves when heated with sulphuric acid with evolution of carbon dioxide and formation of quinoldisulphonic acid (Hesse). Phosphorus chloride converts it into metachlorobenzoyl chloride (Gräbe):

$$C_7H_{12}O_6 + 5PCl_5 = C_7H_4Cl_2O + 5POCl_3 + 8HCl.$$

It is converted by the animal organism into hippuric acid (Lautemann).

The whole behaviour of quinic acid points to the fact that it belongs to the aromatic addition-products.[7] It is tetrahydroxy-hexhydrobenzoic acid, and, since it is optically active, must contain an asymmetric carbon atom, so that it has the following constitution:



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[1] Hesse, *Ann. Chem. Pharm.* cxiv. 292.

[2] Hesse, *ibid.* cc. 239.

[3] Gräbe, *ibid.* cxxxviii. 203.

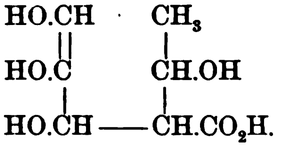
[4] Hesse, *loc. cit.*

[5] Fittig and Hillebrand, *ibid.* cxciii. 197.

[6] *Ibid.* cxxv. 9.

[7] Gräbe, *Ann. Chem. Pharm.* cxlvi. 66.

It differs from quercitol (Part III. p. 194) in containing a carboxyl in the place of one hydroxyl. A different formula has been proposed by Lieben, who found that quinic acid yields iodoform when treated with iodine and caustic potash; he therefore assumes that its constitution must be expressed by the following or some similar formula:[1]



$$\begin{array}{lcl} HO.CH & & CH_3 \\ \| & & | \\ HO.C & & CH.OH \\ | & & | \\ HO.CH & \text{——} & CH.CO_2H. \end{array}$$

The Quinates. The salts of quinic acid are for the most part readily soluble in water, slightly in alcohol, and crystallize well. They have been investigated by Baup,[2] Woskrensky, Hesse, and Clemm.[3]

Sodium quinate, $C_7H_{11}O_6Na + 2H_2O$, crystallizes in large, nacreous, rhombic prisms.

Clemm was unable to obtain the potassium and ammonium salts in crystals; their solutions only gave syrupy residues on evaporation over sulphuric acid.

Calcium quinate, $(C_7H_{11}O_6)_2Ca + 10H_2O$, forms silky, rhombic plates, or long, concentrically-grouped prisms, which dissolve at 10° in 6 parts of water and are insoluble in absolute alcohol.

Barium quinate, $(C_7H_{11}O_6)_2Ba + 6H_2O$, crystallizes, according to Henry and Plisson, in acute octohedral pyramids, while Baup always obtained it in dodecahedra formed by the combination of two pointed pyramids, and Clemm only as a partially crystalline mass.

Lead quinate, $(C_7H_{11}O_6)_2Pb$, crystallizes in readily soluble needles; ammonia added to its solution produces a voluminous, hydrated precipitate which has the formula $C_7H_8O_6Pb_2$, after drying at 200°.

Silver quinate, $C_7H_{11}O_6Ag$, forms warty crystals, which readily dissolve in water and blacken in the light.

Copper quinate, $(C_7H_{11}O_6)_2Cu + 5H_2O$, crystallizes in light blue plates.

Basic copper quinate, $C_7H_{10}O_6Cu + 2H_2O$, is obtained by boiling the aqueous solution of the acid with an excess of copper oxide it forms small, green crystals, which are only slightly soluble in cold water.

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[1] *Ann. Chem. Pharm.* Suppl. vii. 232.

[2] *Ibid.* vi. 1; *Ann. Chim. Phys.* [2] li. 56.

[3] *Ann. Chem. Pharm.* cx. 345.

Ethyl quinate, $C_6H_7(OH)_4CO_2.C_2H_5$, was obtained by Hesse by the action of ethyl iodide on the silver salt; it is a viscid mass, which is readily soluble in water and alcohol, and has a very bitter taste.

Ethyl tetracetylquinate, $C_6H_7(OCO.CH_3)_4CO.OC_2H_5$, is formed by boiling the ethyl ether with acetic anhydride, and crystallizes from boiling water in plates; it separates from ether in large, rhombic crystals which melt at 135°, and sublime without decomposition (Fittig and Hilldebrand).

THE XYLENE GROUP.

2208 It has been already mentioned under benzene (Part III. p. 66) that Mansfield in 1848 discovered that coal-tar naphtha contains, besides benzene, its homologues; of these he isolated the following (C = 6):

	Boiling-point.
Toluol, $C_{14}H_8$	about 113°.
Cumol, $C_{18}H_{12}$	143°—145°.
Cymol, $C_{20}H_{14}$	170°—172°.

He adds, it is interesting to note, "that tar-oil contains among its constituents the only four known members of the series $C_6 + n(C_2H_2)$. It seems, therefore, not improbable that the gap which still exists in this series (n = 5), corresponding to a substance whose boiling-point lies between those of toluol and cumol, will be filled by a compound to be obtained from tar-oil.[1]

Soon after this, Cahours discovered xylol (*xylène*),C_8H_{10}(C = 12), boiling at 128°—130°, along with toluol in crude wood-spirit (ξύλον, wood),[2] and Völkel found the same hydrocarbons in wood-tar.[3] Church then stated that xylol is also contained in coal-tar oil, and boils at 126·2°,[4] whereas Ritthausen[5] and Hiltenkamp[6] could only detect in it the hydrocarbons already discovered by Mansfield.

Warren de la Rue and H. Müller then showed that Rangoon tar contains benzol and its homologues, which they were unable to isolate, but recognised by conversion into their characteristic nitro-compounds.[7] Shortly before this time, Bussenius and Eisenstuck had investigated the rock oil from ehnde in Hanover, and discovered in it a new hydrocarbon, hich they called petrol, C_8H_{10}, its existence being proved by its haracteristic trinitro-derivative;[1] and Hugo Müller then showed hat the hydrocarbon obtained from coal-tar and boiling at 140° s not cumol, but xylol, which also occurs in the oils from urmah and Sehnde, trinitropetrol being identical with trinitroylol.[2] In spite of this Béchamp repeated the statement that ylol boils at 126°—130°, adding that coal-tar also contains a new" hydrocarbon boiling at 139°—140°.[3]

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[1] *Ann. Chem. Pharm.* lxix. 162.

[2] *Ibid.* lxxiv. 168; lxxvi. 286.

[3] *Ibid.* lxxxvi. 331.

[4] *Phil. Mag.* [4] ix. 256.

[5] *Journ. Prakt. Chem.* lxi. 74.

[6] *Ann. Chem. Pharm.* xcv. 83.

[7] *Journ. Prakt. Chem.* lxx. 300.

Mansfield's cumol was subsequently proved to be a mixture f trimethylbenzenes.

After Fittig and Tollens had made the important discovery that the synthetic methylphenyl or methylbenzol is identical with toluol,[4] it was supposed that ethylphenyl or ethylbenzol would be identical with xylol. This, however, was found not to be the case, since it boils as much as 7° lower than the latter, and does not yield a crystallized trinitro-derivative.

Beilstein then investigated xylol more carefully; he fully confirmed Müller's observations and found that on oxidation with chromic acid it yields dibasic terephthalic acid, $C_8H_6O_4$.[5] About this time Fittig prepared methylbenzyl, which he considered to be identical with xylol, by the action of sodium on a mixture of bromotoluol and methyl iodide.[6] He also found that ethylphenyl is easily oxidized to benzoic acid and that its derivatives are completely different from those of xylol.[7]

Glinzer and Fittig then undertook a careful examination of methylbenzyl, or, as they now termed it, methyltoluol; like xylol it yielded terephthalic acid on oxidation, but the trinitroderivatives proved to have different properties.[8] A further investigation of the oxidation products of xylol showed that toluic acid, the next homologue of benzoic acid,[9] is first formed, and this was also obtained from methyltoluol. In spite of this, however, the hydrocarbons were shown to be different, as the properties of their substitution products did not agree.[10]

Fittig and Velguth then obtained a third isomeric hydrocarbon, which they named isoxylol, by heating monobasic mesitylenic acid, $C_6H_3(CH_3)_2CO_2H$, prepared by the oxidation of mesitylene,

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[1] *Ann. Chem. Pharm.* cxiii. 151.

[2] *Zeitschr. Chem.* 1864, 161.

[3] *Compt. Rend.* lix. 47.

[4] *Ann. Chem. Pharm.* cxxxi. 303.

[5] *Ibid.* cxxxiii. 32.

[6] *Ibid.* cxxxiii. 47.

[7] *Ibid.* cxxxiii 222.

[8] *Ibid.* cxxxvi. 303.

[9] Yssel de Schepper and Beilstein, *ibid.* cxxxvii. 301.

[10] Fittig, Ahreus and Mattheides, *ibid.* cxlvii. 15.

me of concentrated nitric acid and two or three volumes , the ortho- and para-compounds being thus oxidized to esponding toluic acids, $C_6H_4(CH_3)CO_2H$, or their nitro- ves, while the meta-compound is scarcely attacked. he evolution of red fumes ceases, the liquid is distilled eam and the distillate agitated with caustic soda, washed ater, dried and distilled.[1]

order to estimate the amounts of the three isomerides itatively, 100 c.c. of the crude xylene are boiled for half our to an hour with a mixture of 40 c.c. of nitric acid . gr. 1·4 and 60 c.c. of water, the whole being repeatedly ted. The unattacked portion is then washed with caustic and distilled with steam, the distillate is measured and en up with 1·5 vols. of concentrated sulphuric acid, the xylene being thus dissolved, while the paraffins remain nd and are measured in a graduated cylinder.

he amount of paraxylene is found by thoroughly agitating c.c. of the crude xylene with 120 c.c. of concentrated sul- ric acid for half an hour, a mixture of paraffins and para- ene being left undissolved; this is then treated with an al volume of fuming sulphuric acid, containing 20 per cent. trioxide, which dissolves out the paraxylene. The amounts paraxylene, metaxylene and paraffins are thus directly asured, the difference from 100 c.c. being that of the thoxylene.

In this way Levinstein has found in various samples of crude nglish and Scotch xylene:[2]

Paraxylene	3—10 per cent.
Metaxylene	70—87 "
Orthoxylene	2—15 "
Paraffins	3—10 "

ccording to Reuter these methods of separation are not accurate, nce nitric acid of the concentration employed also attacks etaxylene, and paraxylene dissolves in ordinary sulphuric acid, though to a much smaller extent than its isomerides. The sistance of the xylenes to the action of acids is, however, nsiderably increased by the presence of paraffins.[3]

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[1] Fittig and Velguth, *Ann. Chem. Pharm.* cxlviii. 10; Tawildarow, *Zeitschr. em.* 1870, 418; Brückner, *Ber. Deutsch. Chem. Ges.* ix. 405.

[2] *Ibid.* xvii. 444.

[3] *Ibid.* xvii. 2028.

When a mixture of the three xylenes is treated with bromine containing 1 per cent. of iodine, they are converted into the tetrabromoxylenes, $C_6Br_4(CH_3)_2$, which yield the tetrabromophthalic acids quantitatively when heated with bromine and water to 160°—170°:

$$C_6Br_4(CH_3)_2 + 6Br_2 + 4H_2O = C_6Br_4(CO_2H)_2 + 12HBr.$$

Since these can readily be separated, the composition of the original mixture can be determined in this way.[1]

THE XYLENES, OR DIMETHYLBENZENES, $C_6H_4(CH_3)_2$.

2209 *Orthoxylene*, (1 : 2), was first prepared pure by the distillation of paraxylic acid, $C_6H_3(CH_3)_2CO_2H$, with lime;[2] it is also formed by the action of sodium on a mixture of orthobromotoluene and methyl iodide,[3] and when a hot mixture of toluene and aluminium chloride is treated with methyl chloride. A small quantity of paraxylene is always formed in this reaction, together with still less metaxylene and a larger amount of the isomeric trimethylbenzenes.[4] It has also been prepared from cantharidin, $C_{10}H_{12}O_4$, which is the characteristic constituent of Spanish flies, and yields pure orthoxylene when heated with phosphorus pentasulphide.[5]

It is a liquid which boils at 142°—143°, solidifies in a freezing mixture to crystals, melting at −28°,[6] and is oxidized to orthotoluic acid by heating with dilute nitric acid, while chromic acid produces complete combustion. When agitated with a boiling solution of potassium permanganate, however, it yields phthalic acid.[7] A cold mixture of nitric and sulphuric acids converts it into liquid nitro-derivatives, and a single drop of orthoxylene can thus be distinguished from the para- and meta-compounds.[8]

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[1] Friedel and Crafts, *Compt. rend.* ci. 1218.

[2] Bieber and Fittig, *Ann. Chem. Pharm.* clvi. 238.

[3] Hübner and Jannasch, *ibid.* clxx. 117; Reymann, *Bull. Soc. Chim.* xxvi. 532.

[4] Jacobsen, *Ber. Deutsch Chem. Ges.* xiv. 2624.

[5] Piccard, *ibid.* xii. 580.

[6] Colson, *Ann. Chim. Phys.* [6] vi. 128.

[7] Claus and Pieszcek, *Ber. Deutsch. Chem. Ges.* xix. 3083.

[8] Jacobsen, *ibid.* xix. 2518.

Dihydro-orthoxylene, or *Cantharene*, $C_6H_6(CH_3)_2$. The compound $C_{10}H_{12}I_2O_3$ is formed by the action of hydriodic acid on cantharidin, and is converted into cantharene by heating with concentrated caustic potash; the latter boils at 134°, smells like camphor and oil of turpentine, rapidly absorbs oxygen from the air and is oxidized to orthotoluic acid by dilute nitric acid.[1]

Metaxylene (1 : 3) may be obtained pure by heating xylic acid $C_6H_3(CH_3)_2CO_2H$ (Bieber and Fittig), or the isomeric mesitylenic acid (Fittig and Velguth) with lime, and by the action of sodium on a mixture of methyl iodide and meta-iodotoluene.[2] It boils at 139·8° and has a specific gravity of 0·8780 at 0°, and of 0·8660 at 15°; it solidifies when strongly cooled and then melts at $-54°$ to $-53°$.[3] It is only attacked with difficulty by dilute nitric acid, even on boiling; when, however, it is boiled for several hours with nitric acid of specific gravity 1·4, diluted with one and a half times its volume of water, metatoluic acid is obtained (Reuter), while chromic acid solution oxidizes it to isophthalic acid, which is also formed, together with metatoluic acid, by the action of potassium permanganate.[4]

Metaxylene, as already mentioned, occurs in various tars and petroleums, and it has also been found in that from the Caucasus.[5] It forms a characteristic trinitro-derivative, which is only slightly soluble in alcohol and yields nitrodiamidometaxylene (p. 409) on partial reduction. These reactions serve to detect small quantities of metaxylene in petroleum, &c.

Tetrahydrometaxylene, $C_6H_8(CH_3)_2$, is formed when camphoric acid, $C_8H_{14}(CO_2H)_2$, is heated to 200° with concentrated hydriodic acid,[6] and has also been prepared from oxycamphoric acid, under which it will be mentioned. It is a liquid which boils at 119°, and is converted into trinitrometaxylene by a mixture of nitric and sulphuric acids.

Hexhydrometaxylene, $C_6H_{10}(CH_3)_2$, is obtained by heating camphoric acid or metaxylene with hydriodic acid to 280°. It occurs in Baku petroleum (Beilstein and Kurbatow) and in essence of resin (Renard); it boils at 116°—120°, and also yields trinitrometaxylene with nitric and sulphuric acids.[7]

Paraxylene (1 : 4) is formed by the action of sodium on a

[1] Piccard, *Ber. Deutsch. Chem. Ges.* xix. 1406.

[2] Wroblewsky, *Ann. Chem. Pharm.* cxcii. 200.

[3] Colson, *loc. cit.*

[4] Claus and Burstert, *Ber. Deutsch. Chem. Ges.* xix. 3084.

[5] Doroschenko, xviii. Ref. 662; Markownikow, *Ann. Chem. Pharm.* ccxxxiv. 89.

[6] Wreden, *Ann. Chem. Pharm.* clxxxvii. 171.

[7] *Ibid.* clxxxvii. 151.

mixture of methyl iodide and parabromotoluene[1] or paradibromobenzene.[2] It boils at 136°—137°, and has a specific gravity [illegible] when strongly cooled it solidifies to rhombic prisms resembling heavy spar,[3] which melt at + 15°. Dilute nitric acid oxidizes it to paratoluic acid, while chromic acid or potassium permanganate give terephthalic acid.

Paraxylene occurs in the petroleum from Galicia along with metaxylene.[4]

[illegible] $C_6H_{10}(CH_3)_2$, is obtained by heating mono[illegible] with zinc chloride to 150°—160°, and [illegible] boiling at [illegible], which is converted into trinitroparaxylene by nitric and sulphuric acids.[5]

SUBSTITUTION PRODUCTS OF THE XYLENES.

[illegible] When one atom of hydrogen is replaced in the aromatic [illegible] isomeric compounds may be formed. Metaxylene yields three, which are distinguished as symmetric = s, asymmetric = a and adjacent [illegible] = v. Two, asymmetric = a, and adjacent = v are derived from orthoxylene, while paraxylene [illegible] which has therefore received no more particular designation.

HALOGEN SUBSTITUTION PRODUCTS OF THE XYLENES.

v-*Chlororthoxylene*, $C_6H_3(CH_3)_2Cl$ (1 : 2 : 3), is formed, together with the following compound, when orthoxylene, to which 5 per cent. of iodine has been added, is treated with chlorine at 0°. In order to separate the two isomerides, they are converted into the sulphonic acids, the pure sodium salts of which are then decomposed by heating with concentrated hydrochloric acid. Adjacent chlororthoxylene is a liquid boiling at 189·5°.

a-Chlororthoxylene (1 : 2 : 4) boils at 191·5° and, like its isomeride, remains liquid at − 20°.[6]

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[1] Fittig and Glinzer, *Ann. Chem. Pharm.* cxxxvi. 303.
[2] V. Meyer, *Ber. Deutsch. Chem. Ges.* iii. 753; Jannasch, *ibid.* x. 1356.
[3] Jacobsen, *ibid.* xvii. 2379.
[4] Palewski, *ibid.* xviii. 1915.
[5] R. Schiff, *ibid.* xiii. 1408.
[6] Krüger, *ibid.* xviii. 1755.

The chlororthoxylenes are converted by oxidation into the corresponding chlorotoluic and chlorophthalic acids.

According to Claus and Kautz, only one chlororthoxylene is formed, which boils at 205° and yields the following compounds on further chlorination:[1]

	Melting-point.	Boiling-point.
Dichlororthoxylene, $C_6H_2Cl_2(CH_3)_2$, crystalline mass	+ 3°	227°
Trichlororthoxylene, $C_6HCl_3(CH_3)_2$, lustrous needles	93°	265°
Tetrachlororthoxylene, $C_6Cl_4(CH_3)_2$, long needles	215°	—

a-Chlorometaxylene, $C_6H_3(CH_3)_2Cl(1:3:4)$, is formed when metaxylene is chlorinated at 0° in presence of iodine; the crude product, which distils between 185°—188°, is purified by converting it into the sulphonic acid and then preparing the sodium salt or *chlorometaxylenesulphamide*, $C_6H_2(SO_2.NH_2)Cl(CH_3)_2$, from this. The latter crystallizes from hot alcohol in hard, compact, lustrous prisms melting at 195°. Both of these compounds yield pure chlorometaxylene when heated with hydrochloric acid. It boils at 186·5° and does not solidify at − 20°; it is oxidized to chlorometatoluic acid by chromic acid, while it is converted into ortho-homoparahydroxybenzoic acid by fusion with caustic potash.[2]

Chloroparaxylene, $C_6H_3(CH_3)_2Cl(1:4:2)$, is obtained in a precisely similar manner to chlorometaxylene; it boils at 186° and solidifies in a freezing mixture to a crystalline mass, which melts at + 2°.

Dichloroparaxylene, $C_6H_2(CH_3)_2Cl_2$, is only slightly soluble in cold, readily in hot alcohol, and crystallizes in flat needles or plates; it melts at 71° and boils at 221°.[3]

a-Bromorthoxylene, $C_6H_3(CH_3)_2Br(1:2:4)$, is formed by the direct bromination of orthoxylene in the cold in the presence of iodine, no isomeride being produced,[4] and more slowly when bromine alone is allowed to act in the dark, orthoxylyl bromide being obtained in the sunlight[5] It boils at 214·5° and solidifies below 0° to a fibrous, crystalline mass, melting at − 0·2°. When heated with ethyl chloroformate and sodium amalgam, paraxylic acid, $C_6H_3(CH_3)_2CO_2H$, is formed.

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[1] Jacobsen, *Ber. Deutsch. Chem. Ges.* xviii. 1367.

[2] *Ibid.* xviii. 1760.

[3] Kluge, *ibid.* xviii. 2098.

[4] Jacobsen, *ibid.* xvii. 2372.

[5] Schramm, *ibid.* xviii. 1278.

The following compounds are formed by the further action of bromine (Jacobsen):

Solid dibromorthoxylene, $C_6H_2(CH_3)_2Br_2$ (1 : 2 : 4 : 5), crystallizes from hot alcohol in large, rhombic plates, which melt at 88°; it readily sublimes in very large, thin plates, boils at 278° and yields symmetric tetramethylbenzene, $C_6H_2(CH_3)_4$, on treatment with sodium and methyl iodide.

Liquid dibromorthoxylene boils at 277° and solidifies in the cold to a hard crystalline mass, melting at + 6·8°.

Tetrabromorthoxylene, $C_6(CH_3)_2Br_4$, is formed when orthoxylene is allowed to drop into bromine containing 1 per cent. of aluminium bromide, the whole being kept at 0°.[1] It is very sligbtly soluble in alcohol, readily in benzene, and crystallizes in long, lustrous needles, which melt at 262°, or according to Blümlein at 254°—255°, and boil at 374°—375°.

Jacobsen was unable to prepare tribromorthoxylene pure.

α-Bromometaxylene, $C_6H_3(CH_3)_2Br$ (1 : 3 : 4), is prepared like the ortho-compound; it is a liquid, which boils at 203°—204°, and is converted into the corresponding bromotoluic acid by oxidation,[2] while xylic acid is formed by the action of carbon dioxide and sodium.[3]

s-Bromometaxylene, (1 : 3 : 5), has been prepared from brominated metaxylidine by the diazo-reaction. It boils at 204°, remains liquid at −20°, and is converted into symmetric dimethylethylbenzene by sodium and ethyl bromide.[4]

α-Dibromometaxylene, $C_6H_2(CH_3)_2Br_2$, is formed when metaxylene is allowed to stand in contact with an excess of bromine for twenty-four hours, the liquid being kept cool.[5] It crystallizes from alcohol in colourless, nacreous plates, boils at 255°—256°, and melts at 72°.[6]

β-Dibromometaxylene was obtained by Wroblewsky, together with his monobromoxylene, as a liquid which boils at 252° and does not solidify at −20°.

Tetrabromometaxylene, $C_6(CH_3)_2Br_4$, is formed when metaxylene is allowed to stand for a long time in contact with a large excess of bromine. It is scarcely soluble in cold, slightly in boiling alcohol, but dissolves readily in benzene, and crystallizes in fine needles which melt at 241° (Fittig and Bieber).

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[1] Blümlein, *Ber. Deutsch. Chem. Ges.* xvii. 2492.

[2] Fittig, *Ann. Chem. Pharm.* cxlvii. 31.

[3] Kekulé, *ibid.* cxxxvii. 186.

[4] Wroblewsky, *ibid.* cxcii. 115.

[5] Fittig, Ahrens and Mattheides, *ibid.* cxlvii. 24.

[6] Fittig and Bieber, *ibid.* clvi. 236.

Bromoparaxylene, $C_6H_3(CH_3)_2Br$ (1 : 4 : 2), is prepared by the action of bromine on cooled paraxylene in the presence of iodine, and is also formed when bromine is allowed to act alone in the dark (Schramm). It is a liquid, which boils at 205·5°, and sometimes solidifies when strongly cooled, but frequently remains liquid until a crystal of the solid compound has been added, when it forms plates or tablets, melting at + 9°.[1]

Dibromoparaxylene, $C_6H_2(CH_3)_2Br_2$ (1 : 4 : 2 : 5), boils at 261°, and crystallizes from alcohol in large plates or flat needles, melting at 75·5°. When these are allowed to remain in the mother liquor they are converted into transparent, asymmetric crystals, which closely resemble regular octohedra (Jacobsen). It is converted into symmetric tetramethylbenzene by the action of sodium and methyl iodide.[2]

In addition to this compound, a liquid dibromoparaxylene, which boils at 260°—264° and solidifies in a freezing mixture, is formed in small quantity.

A tribromoparaxylene was not formed when the necessary quantity of bromine was added, the following substance being obtained together with the preceding compounds:

Tetrabromoparaxylene, $C_6(CH_3)_2Br_4$, is very slightly soluble in alcohol, and crystallizes from hot toluene in long, fine needles, melting at 253°.

NITRO-SUBSTITUTION PRODUCTS OF THE XYLENES.

2211 *v-Nitro-orthoxylene*, $C_6H_3(CH_3)_2NO_2$ (1 : 2 : 3), is formed, together with the following compound, when orthoxylene is treated in a freezing mixture with concentrated nitric and sulphuric acids; it is a liquid, which boils at 245°—247°.[3]

a-Nitro-orthoxylene (1 : 2 : 4) is almost the sole product when pure nitric acid is employed; it crystallizes from alcohol in long, brittle, light yellow, lustrous prisms, melts at 290° and boils at 280°.[4]

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[1] Jannasch, *Ann. Chem. Pharm.* clxxi. 82; Jacobsen, *Ber. Deutsch. Chem. Ges.* xviii. 356.

[2] Jannasch, *ibid.* x. 1357.

[3] Nölting and Forel, *ibid.* xviii. 2669.

[4] *Ibid.* xvii. 159.

Dinitro-orthoxylene, $C_6H_2(CH_3)_2(NO_2)_2$, is formed, together with the following compound when orthoxylene is heated for a considerable time to 100° with a mixture of nitric and sulphuric acids. It crystallizes from boiling alcohol in long, lustrous needles, melting at 71°.

Trinitro-orthoxylene, $C_6H(CH_3)_2(NO_2)_3$, forms white, lustrous scales, which melt at 178°, and are almost insoluble in alcohol.[1]

v-Nitrometaxylene (1 : 3 : 2) is obtained by the action of nitric and sulphuric acids on metaxylene in the cold.[2] It has been prepared pure from the corresponding nitrometaxylidine by the diazo-reaction.[3] It is a liquid boiling at 225°.

a-Nitrometaxylene (1 : 3 : 4) is formed in the preparation of the preceding compound, and in preponderating amount when pure, well-cooled nitric acid is employed. It is a light yellow liquid, which boils at 238° and does not solidify at – 20°.[4]

s-Nitrometaxylene (1 : 3 : 5) is obtained from nitro-a-metaxylidine by dissolving it in absolute alcohol, adding two molecules of sulphuric acid, and then treating the well-cooled liquid with twice the theoretical quantity of ethyl nitrite in order to prevent the formation of the diazo-amido-compound. The liquid is heated to boiling after standing for some time, the alcohol driven off and the remainder distilled with steam.

s-Nitrometaxylene boils at 263°, and crystallizes from alcohol in large, flat needles, melting at 74°—75°.[5]

s-Dinitrometaxylene, $C_6H_2(CH_3)_2(NO_2)_2$ (1 : 3 : 4 : 6), is readily prepared by heating metaxylene with fuming nitric acid; it crystallizes from hot alcohol in large, flat, colourless needles or lustrous prisms, melting at 93°.[6]

v-Dinitrometaxylene (1 : 3 : 4 : 2) is formed together with its isomerides when xylene is nitrated at a low temperature with a mixture of nitric and sulphuric acids; it is readily soluble in alcohol, and crystallizes in scale-like plates, melting at 83°.[7]

Trinitrometaxylene, $C_6H(CH_3)_2(NO_2)_3$ (1 : 3 : 2 : 4 : 6). This characteristic compound, which has been previously mentioned

[1] Drossbach. *Ber. Deutsch. Chem. Ges.* xix. 2156.

[2] Nölting and Forel, *Ber. Deutsch. Chem. Ges.* xviii. 2668.

[3] Grevingk, *ibid.* xvii. 2430.

[4] Tawildarow, *Zeitschr. Chem.* 1870, 418; Harmsen, *Ber. Deutsch. Chem. Ges.* xiii. 1558.

[5] Wroblewsky, *Ann. Chem. Pharm.* ccvii. 91; Thöl, *Ber. Deutsch. Chem. Ges.* xviii. 359; Nölting and Forel.

[6] Fittig, *Ann. Chem. Pharm.* cxlvii. 16; cxlviii. 5.

[7] Grevingk, *Ber. Deutsch. Chem. Ges.* xvii. 2422.

(p. 387), is formed when metaxylene or the preceding compounds are heated with a mixture of nitric and sulphuric acids. It is scarcely soluble in cold, very slightly in boiling alcohol, and crystallizes in fine, flat, colourless needles, melting at 176°.[1]

Nitroparaxylene, $C_6H_3(CH_3)_2NO_2$, is obtained by allowing the calculated quantity of fuming nitric acid to drop into well-cooled paraxylene. It is a yellow liquid, which boils at 239° and does not solidify at – 20°.[2]

a-Dinitroparaxylene, $C_6H_2(CH_3)_2(NO_2)_2$ (1 : 4 : 2 : 6), is formed, together with its isomerides, when paraxylene is dissolved in cold, fuming nitric acid. It crystallizes from alcohol in very thin, lustrous needles, melting at 124°, and is deposited from glacial acetic acid in long, broad needles.

β-Dinitroparaxylene (1 : 4 : 2 : 3) is more readily soluble in alcohol, and crystallizes on gradual evaporation in monoclinic tablets, which resemble crystals of calcspar, and melt at 93°.[3] It is a characteristic property of these two nitroxylenes that equal molecules of them combine to form a double compound, which can be crystallized from glacial acetic acid, but is decomposed by alcohol into its constituents.[4] It forms transparent monoclinic prisms with sphenoid faces, and melts at 99·5°.

γ-Dinitroparaxylene (1 : 4 : 2 : 5) is slightly soluble in cold, more readily in hot alcohol, and forms long, yellow needles with a vitreous lustre, which melt at 147°—148°.[5]

Lellmann determined the constitutions of these three isomerides by the methods already described (Part III., p. 245); the first two, which are formed in largest quantity, were converted into the hydrochlorides of the corresponding diamines, their solutions evaporated with ammonium thiocyanate, and the residues heated to 120°, ground up with water, washed, dissolved in caustic soda and these solutions heated with lead acetate. The *a*-compound gave a precipitate of lead sulphide while the *β*-compound did not, and was thus proved to be an orthodiamine.

He then prepared the free *a*-diamidoparaxylene, which is a crystalline mass, and combines with allyl mustard oil to form the compound $C_6H_2(CH_3)_2(NH.CS.NH.C_3H_5)_2$, which crystallizes in small needles, melting without decomposition at 112·5°. It is therefore a metadiamine, and the γ-compound must, accordingly, contain the nitroxyl groups in the para-position.

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[1] Luhmann, *Ann. Chem. Pharm.* cxliv. 276 ; Fittig, *loc. cit.* ; Grevingk, *loc cit.*

[2] Jannasch, *Ann. Chem. Pharm.* clxxvi. 55 ; Nölting and Forel, *loc. cit.*

[3] Fittig and Glinzer, *Ann. Chem. Pharm.* cxxxvi. 307 ; Fittig, Ahrens and Mattheides, *ibid.* cxlvii. 17.

[4] Jannasch and Stünkel, *Ber. Deutsch. Chem. Ges.* xiv. 1146.

[5] Lellmann, *Ann. Chem. Pharm.* ccxxviii. 250.

Trinitroparaxylene, $C_6H(CH_3)_2(NO_2)_3$ (1 : 4 : 2 : 3 : 5), may readily be prepared by nitrating with a mixture of nitric and sulphuric acids, the whole being gently heated at the close of the operation. It crystallizes from alcohol in stellate aggregates of dazzling white needles, which melt at 139°—140°.[1]

XYLENESULPHONIC ACIDS, $C_6H_3(CH_3)_2SO_3H$.

2212 *Orthoxylenesulphonic acid* (1 : 2 : 4) is formed by dissolving orthoxylene in tolerably hot sulphuric acid. It crystallizes from a somewhat dilute acid solution with two molecules of water in long, rectangular tablets or thicker, flat prisms with pointed ends. Its salts crystallize extremely well. When its potassium salt is heated with sodium formate, paraxylic acid is formed.

Sodium orthoxylenesulphonate, $C_6H_2(CH_3)_2SO_3Na + 5H_2O$, separates from a concentrated solution in flat prisms, the size of which seems only to be limited by that of the containing vessel; they soon effloresce on exposure to the air.

Orthoxylenesulphonic chloride, $C_6H_3(CH_3)_2SO_2Cl$, crystallizes from ether in prisms, melting at 51°—52°.

Orthoxylenesulphonamide, $C_6H_3(CH_3)_2SO_2.NH_2$, separates from hot alcohol in prisms, which melt at 144°.[2]

a-Metaxylenesulphonic acid (1 : 3 : 4) is formed, together with a small quantity of the isomeric compound, when metaxylene is dissolved in sulphuric acid. It separates on the addition of a little water in large plates or prisms, which contain two molecules of water. Xylic acid is formed when potassium salt is heated with sodium formate (p. 391).

Sodium metaxylenesulphonate, $C_6H_3(CH_3)_2SO_3Na$, crystallizes from water in scales, and from alcohol in small plates possessing a silver lustre.

a-Metaxylenesulphonic chloride solidifies in the cold to a radiating mass, or to prisms which melt at 34°.

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[1] Fittig and Glinzer; Nölting and Geissmann, *Ber. Deutsch. Chem. Ges.* xix 144.

[2] Jacobsen, *ibid.* x. 1010 ; xi. 22.

a-Metaxylenesulphamide crystallizes from water in long pointed needles and melts at 137°.

v-Metaxylenesulphonic acid (1 : 3 : 2) has not been prepared pure; its calcium salt when heated with sodium formate yields a xylic acid, which decomposes on distillation with lime into carbon dioxide and metaxylene. Its chloride is an oily liquid, and the amide crystallizes in needles, melting at 95°—96.[1]

Paraxylenesulphonic acid is formed when paraxylene is dissolved at a gentle heat in slightly fuming sulphuric acid. It crystallizes with two molecules of water in large plates or very long, flat prisms.

Sodium paraxylenesulphonate, $C_6H_3(CH_3)_2SO_3Na + H_2O$, crystallizes in large, flat, striated prisms, which do not effloresce in the air.

Paraxylenesulphonic chloride forms flat prisms, which melt at 24°—26°

Paraxylenesulphamide is readily soluble in alcohol, slightly in boiling water, from which it crystallizes in splendid, long needles, melting at 147°—148° (Jacobsen).

HYDROXY-XYLENES, OR XYLENOLS, $C_6H_3(CH_3)_2OH$.

2213 After Dusart, Kekulé and Wurtz had shown that sulphonic acids are converted into phenols by fusion with potash, the last-named of these chemists applied the reaction to xylene, and discovered the interesting fact that this hydrocarbon yields two isomeric phenols, a solid and a liquid xylenol. This isomerism is explained by him as due to the different positions of the hydroxyl with relation to the two methyl groups. "This isomerism," he adds, "could, according to Kekulé's beautiful theory, also exist in xylene itself, as a result of a different arrangement of the side chains in the nucleus."[2] After this supposition had been proved correct and these xylenes were known, it was seen that six xylenols must exist, and these have all now been prepared. Jacobsen obtained four of them from the sulphonic acids just described,[1] and the two others have been prepared from the xylidines by means of the diazo-reaction.[2] Like ordinary phenol, they readily form tribromo-derivatives.

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[1] Jacobsen, *Ann. Chem. Pharm.* clxxxiv. 188; *loc. cit.*

[2] *Ann. Chem. Pharm.* cxlvii. 372; see also Wroblewsky, *Zeitschr. Chem.* 1868, 232.

The xylenols also occur in coal-tar. They have not, indeed, been isolated, but their derivatives have been prepared from it.

The tar obtained as a by-product from blast furnaces which are worked with coal seems to be especially rich in xylenols; the creosote oil fraction, boiling at 210°—240°, when distilled over heated zinc dust, yielded a mixture of hydrocarbons, which consisted chiefly of metaxylene.[3]

a-Orthoxylenol (1 : 2 : 4) crystallizes from hot water in very long needles and from very dilute alcohol in rhombic pyramids, melting at 62·5°;[4] it boils at 225° and forms an aqueous solution which is not coloured by ferric chloride.

a-Tribromorthoxylenol, $C_6Br_3(CH_3)_2OH$, crystallizes from alcohol in fine, snow-white, matted needles, melting at 169°.

v-Orthoxylenol (1 : 2 : 3) crystallizes from water in white needles, melts at 75° and boils at 218°; its aqueous solution is coloured blue by ferric chloride, but is not affected by bleaching-powder solution.

a-Metaxylenol (1 : 3 : 4) is, according to Jacobsen, a strongly refractive liquid, which smells like phenol, boils at 211·5° and becomes viscid at −20°, without, however, solidifying. These are also the properties of the liquid xylenol discovered by Wurtz, while Städel and Hölz showed that the xylenol prepared from pure a-metaxylidine solidifies at the ordinary temperature.[5] Jacobsen, on reinvestigation, found that his preparation crystallized after repeated cooling or on the addition of a small crystal.[6] It forms white needles, melting at 26°. It dissolves slightly in water, yielding a solution which is coloured blue by ferric chloride; the alcoholic solution, on the other hand, is coloured a splendid dark green, which passes into blue when water is added.

a-Metaxylenyl methyl ether, $C_6H_3(CH_3)_2OCH_3$, is a liquid which has a faint smell resembling that of benzene, and boils at 192°.

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[1] *Ber. Deutsch. Chem. Ges.* xi. 23.

[2] Thol, *ibid.* xviii. 359, 2561; Nölting and Forel, *ibid.* xviii. 2668.

[3] Smith, Coutts and Brothers, *Journ. Chem. Soc.* 1886, i. 17.

[4] Jacobsen, *Ber. Deutsch. Chem. Ges.* xvii. 161.

[5] *Ber. Deutsch. Chem. Ges.* xviii. 2921.

[6] *Ibid.* xviii. 3463.

a-Metaxylenyl acetate, $C_6H_3(CH_3)_2O.CO.CH_3$, is a liquid boiling at 226°, which has a faint odour of oil of bergamot.

	Melting-point.
a-Bromometaxylenol, $C_8H_8Br.OH$, oily liquid . . .	—
a-Dibromometaxylenol, $C_8H_7Br_2.OH$, fine, colourless needles	73°
a-Tribromometaxylenol, $C_8H_6Br_3.OH$, long, colourless needles	179°.

v-Metaxylenol (1 : 3 : 2) crystallizes in silky plates or long, flat needles, melts at 74·5°, boils at 211°—212°, and gives no colouration with ferric chloride.

v-Tribromometaxylenol crystallizes from hot alcohol in long, light yellow needles, melting at 175°.

s-Metaxylenol (1 : 3 : 5) is deposited from solution in hot water or from sublimation in splendid white needles, melting at 68°. It boils at 219·5°, and gives no colouration with ferric chloride.

s-Tribromometaxylenol crystallizes from alcohol or benzene in fine. white needles, melting at 166°.

Paraxylenol (1 : 4 : 2) has been prepared from paraxylidine ;[1] it melts at 74·5°, sublimes in needles at a slightly higher temperature, boils at 211·5° and crystallizes from hot water or very dilute alcohol in large, flat needles. It gives no colouration with ferric chloride. The solid compound prepared by Wurtz was almost pure paraxylenol.

	Melting-point.
Monobromoparaxylenol, $C_8H_8Br.OH$, colourless, flexible needles	87°
Tribromoparaxylenol, $C_8H_6Br_3.OH$, deep golden yellow needles	175°.

The great similarity existing between para- and v-metaxylenol is somewhat remarkable (Jacobsen).

A xylenol occurs in crude creosote, which boils at 220°, does not crystallize, and on heating with potash and methyl iodide yields a methyl ether, boiling at 200°.[2] This substance is probably a mixture, and, from its high boiling-point, would seem to consist chiefly of a-orthoxylenol.[3]

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[1] Nölting, Witt and Forel, *Ber. Deutsch. Chem. Ges.* xviii. 2664.

[2] Marasse, *Ann. Chem. Pharm.* clii. 75 ; Tiemann and Mendelsohn, *Ber. Deutsch. Chem. Ges.* x. 57.

[3] Nölting, Witt and Forel, *ibid.* xviii. 2664.

Robiquet, by the distillation of aloes with lime, obtained a liquid which he called *aloïsol*. This substance has been shown by Rembold to be a mixture, the portion soluble in alkalis having the composition of a xylenol.[1]

DIHYDROXY-XYLENES. $C_6H_2(CH_3)_2(OH)_2$.

2214 *Homorcinol*, or *Paraxylorcinol* (1:4:2:6), was obtained by Stenhouse from *Usnea barbata* and *Cladonia rangiferina* and named by him *β*-orcin,[2] a name which was subsequently changed by him and Groves into beta-orcinol. It is a decomposition product of the barbatic acid, $C_{19}H_{20}O_7$, which occurs in these lichens.[3] Lamparter has succeeded in obtaining it, together with orcinol, from *Roccella fuciformis*.[4]

Its constitution was determined by Kostanecki, who prepared it from *a*-nitroparaxylidine, by first converting it into nitroxylenol, reducing this to amidoxylenol, and finally passing from this to paraxylorcinol by means of the diazo-reaction.[5]

It is less soluble in water than orcinol, and is deposited in quadratic crystals, melting at 163°. It possesses a slightly sweet taste, boils at 277°—280°, and is coloured red by ammonia in presence of air more rapidly than orcinol. Its aqueous solution gives with ferric chloride a light carmine-red colouration, quite distinct from the purple-red produced with orcinol. Like the latter it yields a red solution with a beautiful green fluorescence when heated with chloroform and caustic soda (Kostanecki).

Nitrosoparaxylorcinol, $C_6H(CH_3)_2(OH)O(NOH)$, is formed by the action of nitrosyl sulphate (Part III. p. 171) on an aqueous solution of paraxylorcinol, as a lustrous, orange-red precipitate, which crystallizes from glacial acetic acid in small, lustrous, red prisms.

Metaxylorcinol (1:3:4:6) is obtained from s-nitro-a-metaxylidine. It is readily soluble in water, has an acid taste, melts at 125° and boils at 276°—279°. It crystallizes from chloroform in brilliant white, monosymmetric plates, which can also be obtained by sublimation. No red colouration is produced by exposure to ammonia and air.[6]

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[1] *Ann. Chem. Pharm.* cxxxviii. 186.

[2] *Phil. Trans.* 1848, 63.

[3] *Ibid.* cciii. 285.

[4] *Ibid.* cxxxiv. 243.

[5] *Ber. Deutsch. Chem. Ges.* xix. 2318.

[6] Pfaff, *ibid.* xvi. 611 and 1135; Kostanecki, *loc. cit.*

Gundelach, by heating chlorometaxylenesulphonic acid to 230°—250° with caustic potash, obtained a dihydroxy-xylene which should be identical with metaxylorcinol, since, according to Jacobsen, the side chains of the sulphonic acid have the following arrangement: $CH_3 : CH_3 : Cl : SO_3H = 1 : 3 : 4 : 6$.[1] It crystallizes in microscopic prisms, which are tolerably soluble in water, melt at 120° and are coloured deep red by ammoniacal air.[2] This compound is probably impure metaxylorcinol.

The following dihydroxy-xylenes have been prepared by the reduction of the xyloquinones:

Paraxyloquinol, or *Hydrophlorone* (1 : 4 : 2 : 5), is readily soluble in alcohol, slightly in boiling water and benzene, and crystallizes in nacreous plates or tablets, which melt at 210° and sublime in long needles. It reduces silver solution and is re-oxidized to the quinone by ferric chloride. The diethyl ether, $C_8H_8(OC_2H_5)_2$, is formed by heating it with ethyl bromide and caustic potash; it forms lustrous plates, which melt at 105°—106°, and have an odour resembling that of peppermint (Städel and Hölz).

Metaxyloquinol (1 : 3 : 2 : 5) sublimes in needles and melts at 149°.

Orthoxyloquinol (1 : 2 : 3 : 6) crystallizes from water in crusts, which melt at 221° with decomposition.

TRIHYDROXY-XYLENES.

2215 *Trihydroxymetaxylene*, $C_6H(CH_3)_2(OH)_3$, is formed by the reduction of hydroxymetaxyloquinone (p. 404) with sulphurous acid. It is tolerably soluble in cold, readily in hot water, and crystallizes in colourless or yellowish transparent tablets, containing a molecule of water, which is lost at 80°, the anhydrous compound melting at 121°—122°. It is reduced to metaxylene when heated with zinc-dust. Oxidizing agents readily convert it into the quinone; if the aqueous solution be merely allowed to evaporate in the air, the quinhydrone crystallizes out in long needles resembling those of potassium permanganate.

Triacetoxymetaxylene, $C_6H(CH_3)_2(O.CO.CH_3)_3$, is obtained by the action of acetyl chloride, and crystallizes from alcohol in colourless, lustrous prisms, which melt at 99°, and sublime without decomposition when carefully heated.

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[1] *Ber. Deutsch. Chem. Ges.* xviii. 1762.

[2] *Bull. Soc. Chim.* xxviii. 343.

THE XYLOQUINONES, $C_6H_2(CH_3)_2O_2$.

2216 *Paraxyloquinone* (1 : 4 : 2 : 5). Rommier and Bouilhon, by oxidizing the fraction of crude cresol boiling between 195°—220° with sulphuric acid and manganese dioxide, obtained two isomeric quinones, $C_8H_8O_2$, and gave to the one, which is formed in larger quantity and melts at 60°—62°, the name of phlorone, and to the other, melting at 125°, that of metaphlorone.[1] According to Gorup-Besanez and v. Rad, phlorone is also formed by the oxidation of wood-tar creosote.[2] Nietzki then obtained paraxyloquinone by the oxidation of crude xylidine and of paradiamidoxylene with potassium dichromate and sulphuric acid, and found that its properties agree with those of metaphlorone;[3] Carstanjen then showed that phlorone is a mixture of toluquinone with paraxyloquinone, and that the latter yields paraxylene on heating with zinc-dust.[4] It is best prepared from paraxylidine in the same way as benzoquinone from aniline.[5]

Paraxyloquinone is only slightly soluble in water and cold alcohol; it crystallizes from hot alcohol in splendid golden-yellow needles, which melt at 123·5° and readily sublime.

Orthoxyloquinone (1 : 2 : 3 : 6) has been prepared from v-orthoxylidine by oxidation; it is slightly soluble in water, more readily in alcohol, and sublimes in yellow needles, which melt at 55°.

Metaxyloquinone (1 : 3 : 2 : 5) is formed by the oxidation of v- and s-metaxylidine, and crystallizes in splendid yellow needles, melting at 73°.

Hydroxymetaxyloquinone, $C_6H(CH_3)_2(OH)O_2$, is formed when diamidomesitylene, $C_6H(CH_3)_3(NH_2)_2$, is distilled with potassium dichromate and dilute sulphuric acid. It crystallizes from hot water or ether in orange-red needles, has a characteristic smell resembling that of benzoquinone, melts at 103°, and sublimes very readily in splendid, lustrous, deep golden-yellow needles. Its aqueous solution is instantly coloured a splendid reddish violet by the addition of any alkaline substance, and this reaction is so delicate that the slightest traces of the quinone can be detected by it. Insoluble carbonates also produce this colouration; thus, if a 0·1 per cent. solution of the quinone be shaken up with calcium carbonate, the colouration produced is so deep that even a thin layer of the liquid appears quite opaque. The presence of calcium carbonate can thus be shown in very small quantities of mineral waters; free carbonic acid does not affect the colouration, so that the quinone forms a valuable indicator for alkalimetry.

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[1] *Compt. Rend.* lv. 214.
[2] *Zeitschr. Chem.* [2] iv. 560 ; *Ann. Chem. Pharm.* cli. 158.
[3] *Ber. Deutsch. Chem. Ges.* xiii. 470.
[4] *Journ. Prakt. Chem.* [2] xxiii. 421.
[5] Nöltin [illegible]r. *Deutsch. Chem. Ges.* xviii. 2668.

It forms salts, which readily decompose on warming or on exposure to the air in presence of an excess of the base. The potassium salt, $C_8H_7(OK)O_2$, crystallizes from hot alcohol in small, black needles, 1 mgrm. of which is sufficient to impart a deep red colour to a litre of water.[1]

AMIDO-DERIVATIVES OF THE XYLENES.

THE AMIDOXYLENES, OR XYLIDINES, $C_6H_3(CH_3)_2NH_2$.

2217 Cahours gave the name of xylidine to the homologue of toluidine and aniline which he obtained from his xylene (p. 386), by nitrating it and submitting the nitroxylene formed to reduction. This substance and the xylidine obtained by Church in the same manner was obviously a mixture of toluidines and xylidines, while that prepared by Deumelandt from xylene boiling at 140° consisted chiefly of a-metaxylidine, as was also the case with that prepared by Hofmann and Martius by heating paratoluidine hydrochloride to 300° with methyl alcohol. It only became possible to obtain the six xylidines after the three xylenes had been obtained in the pure condition and the six nitroxylenes prepared from these. A mixture of them is manufactured on the large scale from tar-xylene, and the purity and composition of commercial xylidine is therefore dependent on that of the latter. Specimens now come into the market containing as much as 25 per cent. of paraxylidine in addition to ordinary metaxylidine.[2]

The commercial product is employed in the manufacture of azo-colours and of the cumidines, $C_6H_2(CH_3)_3NH_2$, which are obtained by heating the hydrochlorides with wood-spirit.

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[1] Fittig and Siepermann, *Ann. Chem. Pharm.* clxxx. 27.

[2] Nölting, Witt and Forel, *Ber. Deutsch. Chem. Ges.* xviii. 2664; Städel and Hölz, *ibid.* xviii. 2919.

v-Orthoxylidine (1 : 2 : 3) is formed when solid dibromorthoxylene is nitrated, the nitrodibromorthoxylene reduced to dibromoxylidine, and the bromine removed by treatment with sodium amalgam and water.[1] It is a liquid which boils at 223°; its hydrochloride is tolerably soluble in water and crystallizes in white needles containing a molecule of water. The sulphate is only slightly soluble.

v-Acetorthoxylide, $C_6H_3(CH_3)_2NH.CO.CH_3$, crystallizes from hot benzene in white needles melting at 134°.[2]

a-Orthoxylidine (1 : 2 : 4) melts at 49° and boils at 226°. It is tolerably soluble in hot water, readily in alcohol, and crystallizes when caused to solidify quickly or when rapidly deposited from solution in transparent vitreous tablets, while it may be obtained by the gradual evaporation of its petroleum-ether solution in thick monoclinic crystals. Its aqueous solution is not coloured by bleaching powder; the solutions of its salts colour pine-wood an intense yellow.

The hydrochloride is readily soluble in water, but only slightly in hydrochloric acid, and crystallizes with one molecule of water in long, very thin prisms.

a-Acetorthoxylide crystallizes from hot water containing a little alcohol in long, thin, vitreous prisms, which melt at 99°.

The base is converted by the diazo-reaction into a-orthoxylenol.[3]

v-Metaxylidine (1 : 3 : 2) was first obtained by Schmitz by heating β-amidomesitylenic acid, $C_6H_2(CH_3)_2(NH_2)CO_2H$, with lime.[4] Grevingk,[5] and Nölting and Forel,[6] then prepared it from v-nitrometaxylene. It is a liquid boiling at 214°.

Its hydrochloride crystallizes in thin, anhydrous, monoclinic plates, which are readily soluble in water.

v-Acetmetaxylide crystallizes from benzene in white needles, which melt at 176·8°. It is not attacked by caustic potash solution, sulphuric acid, or hydrochloric acid, on heating in an open vessel, but is decomposed by the last of these at 150°.

a-Metaxylidine (1 : 3 : 4) has been known for a longer period than any of its isomerides and is therefore also called ordinary metaxylidine. It is formed by the distillation of a-amidomesitylenic acid with lime (Schmitz) and by the reduction of a-nitrometaxylene.[1] It may also be readily obtained from commercial xylidine by converting this into the hydrochloride and purifying by re-crystallization. In order to obtain it perfectly pure, the acetxylide is prepared, purified by re-crystallization, and decomposed with sulphuric acid. The other xylidine can also be easily obtained pure in this way. It is a liquid boiling at 212°.

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[1] Thöl, *Ber. Deutsch. Chem. Ges.* xviii. 2561; Wroblewsky, *ibid.* xviii. 2904, xix. 285; Jacobsen, *ibid.* xviii. 3166.

[2] Nölting and Forel, *ibid.* xviii. 2668.

[3] Jacobsen, *ibid.* xvii. 159.

[4] *Ann. Chem. Pharm.* cxciii. 377.

[5] *Ber. Deutsch. Chem. Ges.* xvii. 2422.

[6] *Ibid.* xviii. 2676.

The hydrochloride is only slightly soluble in cold water, and crystallizes in anhydrous, rhombic tablets; the hydrobromide crystallizes even better, forming splendid prisms (Städel and Hölz).

a-Acetmetaxylide crystallizes from benzene in white needles melting at 129°; impurities cause a considerable lowering of the melting-point.

s-Metaxylidine (1 : 3 : 5) is obtained by the reduction of the corresponding nitroxylene;[2] it is a liquid boiling at 220°. Its hydrochloride and nitrate crystallize in large, anhydrous needles; 4·66 parts of the latter dissolve in 100 parts of water at 13°.

s-Acetmetaxylide crystallizes from alcohol in large, flat needles, melting at 140·5°.

Paraxylidine (1 : 4 : 2) may be prepared in the usual way by the reduction of nitroparaxylene,[3] and also from commercial xylidine; the latter is run into fuming sulphuric acid containing sufficient trioxide to convert the bases into sulphonic acids, the mixture being well stirred and then heated on the water-bath. The solution is allowed to cool and the solid mass pressed under water to separate the metaxylidinesulphonic acid in the crystalline state. The sodium salt of paraxylidinesulphonic acid is then prepared from the mother-liquor by neutralizing it with lime, filtering, removing the calcium with carbonate of soda, and concentrating the filtrate. It separates in splendid, nacreous plates, which are freed from any adhering traces of the readily soluble salt of the metaxylidinesulphonic acid by washing with a little cold water. Pure paraxylidine is then obtained by the dry distillation of the salt.[4]

It is a liquid boiling at 215°; its hydrochloride and nitrate crystallize in flat needles or large tablets, and the sulphate, which is only slightly soluble, forms small plates.

Acetparaxylide crystallizes from hot water or toluene in long lustrous needles, melting at 139°.

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[1] Tawildarow, *Zeitschr. Chem.* 1870, 418; Nölting and Forel, *loc. cit.*

[2] Wroblewsky, *Ann. Chem. Pharm.* ccvii. 95; Thöl, *Ber. Deutsch. Chem. Ges.* xviii. 359; Nölting and Forel, *loc. cit.*

[3] Schaumann, *Ber. Deutsch. Chem. Ges.* xi. 1537; Nölting and Forel. *ibid.* xviii. 2680.

[4] Nölting, Witt and Forel, xviii. 2664.

alcoholic ammonia. It crystallizes from glacial acetic acid in yellow needles, which melt at 202°—203°, and are converted by the diazo-reaction into *a*-dinitroparaxylene.[1]

DIAMINES AND TRIAMINES OF THE XYLENES, $C_6H_2(CH_3)_2(NH_2)_2$.

2219 *a-Diamidometaxylene*, $C_6H_3(CH_3)_2(NH_2)_2$ (1 : 3 : 4 : 5), is formed by the reduction of a-nitro-a-metaxylidine,[2] and amido-azo-a-metaxylene.[3] It crystallizes from hot benzene in small, white plates, which melt at 77°—78°, and are readily soluble in alcohol.

s-Diamidometaxylene (1 3 : 4 : 6) has been prepared from s-dinitrometaxylene and the corresponding nitroxylidene; it sublimes in white crystals, melting at 104°.

v-Diamidometaxylene (1 : 3 : 4 : 2) sublimes in white needles and melts at 64°.

Nitrodiamidometaxylene, $C_6H(CH_3)_2(NH_2)_2NO_2$, is formed by the reduction of trinitrometaxylene with ammonium sulphide and was first described by Bussenius and Eisenstuck as nitro-petroldiamine (p. 387). It is slightly soluble in cold, more readily in boiling water and readily in alcohol, from which it crystallizes in lustrous, ruby-red prisms, an inch in length, which melt at 212°—213°.[4]

Triamidometaxylene, $C_6H(CH_3)_2(NH_2)_3$ (1 : 3 : 2 : 4 : 6), has been obtained by reducing trinitrometaxylene with hydrochloric acid and stannous chloride; it crystallizes in white needles, which decompose at about 140° without melting.

Diamidometaxylene contains the amido-groups in the ortho-position, and gives all the characteristic reactions of the ortho-diamines (Nölting and Forel); the two other diamidometa-xylenes are metadiamines, and therefore yield azo-dyes when their hydrochlorides are treated with sodium nitrite, as does also triamidometaxylene. The colour prepared from v-diamido-metaxylene dyes silk reddish brown, that from s-diamidometa-xylene, yellowish brown, while the derivative of the triamine produces a grey shade of olive. With diazobenzenesulphonic acid, on the other hand, the v-diamine gives a light yellowish red colouring matter, while that from the s-diamine is darker and that from the triamine a dark, red-black. The shades produced on silk, however, are in the inverse relation; the lightest coloured dye gives the darkest shade, then follows that of the s-diamine, while the substance prepared from the triamine dyes an almost pure golden yellow.[1]

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[1] Nölting and Geissmann, *Ber. Deutsch. Chem. Ges.* xix. 144.
[2] Hofmann, *ibid.* ix. 1298.
[3] Nölting and Forel, *ibid.* xviii. 2683.
[4] Fittig and Velguth, *Ann. Chem. Pharm.* cxlviii. 6.

a-Diamidoparaxylene, $C_6H_2(CH_3)_2(NH_2)_2$ (1 : 4 : 2 : 6), sublimes in white needles, melting at 101·5°—102·5°; its hydrochloride gives a brown colouring matter with sodium nitrite; it forms chrysoïdines with diazo-salts and a dye analogous to toluylene-blue (p. 82) with nitrosodimethylaniline.

β-Diamidoparaxylene (1 : 4 : 2 : 3) sublimes in small needles, melting at 75°; sodium nitrite, added to the solution of its hydrochloride, precipitates an azimido-compound (Part III. p. 270),[2] while ferric chloride produces a deep red colouration.

γ-Diamidoparaxylene (1 : 4 : 2 : 5). Nietzki prepared this compound by the action of zinc and hydrochloric acid on the amidoazoxylene, $C_6H_3(CH_3)_2.N_2.C_6H_2(CH_3)_2NH_2$, prepared from commercial xylidine.[3] Nölting and Forel then obtained it from amido-azoparaxylene, and showed that Nietzki's compound consists of amido-azometaparaxylene.[4] It is also formed by the reduction of γ-nitroparaxylidine. It is slightly soluble in cold, readily in hot water and alcohol, but less readily in benzene, from which it crystallizes in white needles, melting at 146·5°—147°. It yields paraxyloquinone on oxidation.

XYLYL COMPOUNDS.

2220 When an atom of hydrogen in the methyl group of one of the xylenes is replaced by another element or radical, compounds of the monovalent radical *xylyl*, $CH_3.C_6H_4.CH_2$, are obtained; this radical has also been called tolyl, because the monobasic acids, $CH_3.C_6H_4.CO_2H$, which correspond to the xylyl alcohols, $CH_3.C_6H_4.CH_2.OH$, and which decompose into toluene and carbon dioxide when heated with lime, have received the name of toluic acids. The term tolyl has, however, been also applied to the group C_7H_7, and it is therefore preferable to designate the derivatives of the xylenes as xylyl compounds.[1]

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[1] Grovingk, *Ber. Deutsch. Chem. Ges.* xvii. 2442.

[2] Nölting and Geissmann, *ibid.* xix. 144.

[3] *Ibid.* xiii. 470.

[4] *Ibid.* xviii. 2685.

The use of this term is open to the objection that the acids, $(CH_3)_2C_6H_3.CO_2H$, are called xylic acids, because they stand to xylene in the same relation as the toluic acids to toluene and benzoic acid to benzene.[2]

In order to avoid this confusion of terms, it has been proposed to give the name of tolyl to the group $CH_3.C_6H_4$ and to designate the xylyl alcohols according to Kolbe's nomenclature as tolyl carbinols,[3] the toluic acids being called tolylformic acids. In the sequel, however, the names which are in general use will be retained.

Chlorine acts upon boiling xylene in the same way as on toluene, substitution taking place in the methyl group. The first xylyl-compounds were obtained from tar-xylene, but they have now been prepared from the pure hydrocarbons.[4]

Bromine acts on the xylenes at the boiling-point in a similar manner;[5] an energetic reaction also takes places in the sunlight, the first product consisting of a mixture of xylyl bromides.[6]

XYLYL ALCOHOLS, $CH_3.C_6H_4.CH_2.OH$.

Orthoxylyl alcohol was prepared by Raymann by the action of sodium amalgam and water on orthotolualdehyde, which he had prepared from the chloride. It is slightly soluble in water, readily in alcohol, and crystallizes in needles, melting at 54°. According to Colson, who prepared it by heating the bromide with water, it melts at 34·2° and boils at 217°.[7]

Metaxylyl alcohol has been obtained both from the acetate and bromide; it is a liquid, which boils at 215° and has a faint odour.

Metaxylyl ethyl ether, $CH_3.C_6H_4.CH_2.O.C_2H_5$, is a liquid and boils at 202°.

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[1] *Jahresb. Chem.* 1866, 605.
[2] Kekulé, *Ann. Chem. Pharm.* cxxxvii. 186.
[3] Beilstein, *Org. Chem.* 1084.
[4] Raymann, *Bull. Soc. Chim.* xxvi. 532; xxvii. 498; Gundelach, *ibid.* xxvi. 43.
[5] Radziszewski and Wispek, *Ber. Deutsch. Chem. Ges.* xv. 1743; xviii. 1279.
[6] Schramm, *ibid.* xviii. 1272.
[7] Colson, *Bull. Soc. Chim.* xliii. 6; *Ann. Chim. Phys.* [6] vi. 115.

Metaxylyl acetate, $CH_3.C_6H_4.CH_2O.CO.CH_3$, was prepared by Volrath by heating the chloride obtained from tar-xylene with silver acetate.[1] Radziszewski and Wispek then prepared it from the pure bromide. It is a liquid which boils at 226° and possesses an aromatic odour resembling that of apples.

Paraxylyl alcohol was obtained by Cannizzaro from paratoluaidehyde by the action of alcoholic potash, and was named *toluenyl alcohol*. It crystallizes in white needles, and is slightly soluble in cold, more readily in hot water, from which it separates in oily drops which solidify to fine needles, melting at 58·5°—59·5° and boiling at 217°. Hydrochloric acid converts it into the liquid chloride.[2]

Paraxylyl ethyl ether is a liquid which has a similar smell to benzyl alcohol and boils at 203° (Radziszewski and Wispek).

Xylyl chlorides, $CH_3.C_6H_4.CH_2Cl$. These compounds are colourless liquids.

	Melting-point.	Boiling-point.
Orthoxylyl chloride	—	197°—199°
Metaxylyl chloride	—	195°—196°
Xylyl bromides, $CH_3.C_6H_4.CH_2Br$.		
Orthoxylyl bromide, rhombic prisms	21°	216°—217°
Metaxylyl bromide, liquid	—	212°—215°
Paraxylyl bromide, long needles	35·5	218°—220°

XYLYLAMINES.

These have been prepared by heating the xylyl chloride from tar-xylene with ammonia,[3] and are therefore more or less pure meta-compounds.

Monoxylylamine, $CH_3.C_6H_4.CH_2.NH_2$, is an oily, alkaline liquid which boils at 196° and smells strongly of herring brine; its hydrochloride is readily soluble in water and alcohol, and crystallizes in needles.

Dixylylamine, $(CH_3.C_6H_4.CH_2)_2NH$, is a similar liquid, which decomposes above 210°; its hydrochloride forms white needles, which are only slightly soluble in cold, readily in hot water and alcohol.

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[1] *Ann. Chem. Pharm.* cxliv. 261.

[2] *Ibid.* cxxiv. 252.

[3] Jannasch, *ibid.* cxlii. 303; Pieper, *ibid.* cli. 129.

Trixylylamine, $(CH_3.C_6H_4.CH_2)_3N$, is a thick, colourless oil, which has a characteristic odour and a faint alkaline reaction. The hydrochloride crystallizes in loose groups of needles, which are insoluble in water, but slightly soluble in cold and readily in hot alcohol. It decomposes into xylyl chloride and dixylylamine hydrochloride when heated in a current of hydrochloric acid gas.

THE TOLUALDEHYDES.

2221 Chromyl chloride combines with the xylenes, as with benzene and toluene, to form compounds which are decomposed by water with formation of the tolualdehydes.[1]

$$3CH_3.C_6H_4CH(OCrCl_2.OH)_2 + 3H_2O =$$
$$3CH_3.C_6H_4.CHO + 2CrO_3 + Cr_2(OH)_6 + 6HCl.$$

Orthotolualdehyde was first prepared by boiling orthoxylyl chloride with water and lead nitrate; it is a yellowish, strongly refractive liquid, which smells like benzaldehyde and boils at 200°.[2]

Metatolualdehyde has been obtained in a similar manner from metaxylyl chloride;[3] it possesses a similar smell and boils at 199°. It combines with phenylhydrazine to form *metaxylidenehydrazine*, $CH_3.C_6H_4.CH.N_2H.C_6H_5$, which crystallizes from alcohol in thick, yellow prisms, melting at 91°.

Orthonitrometatolualdehyde, $CH_3.C_6H_3(NO_2)CHO$, is formed when the aldehyde is allowed to drop into a cold mixture of nitric and sulphuric acids. It is a yellowish liquid, volatile with steam, and is converted into methylindigo when warmed with caustic soda and acetone.[4]

Paratolualdehyde was prepared by Cannizzaro by the distillation of a mixture of calcium formate and calcium paratoluate, and is a liquid which boils at 204° and possesses a smell resembling that of peppermint.[5]

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[1] Étard, *Ann. Chim. Phys.* [5] xxii. 218, 1881; Bornemann, *Ber. Deutsch. Chem. Ges.* xvii. 1462.

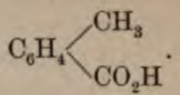
[2] Raymann, *Bull. Soc. Chim.* xxvii. 498.

[3] Lauth and Grimaux, *ibid.* vii. 234; Gundelach, *ibid.* xxvi. 44.

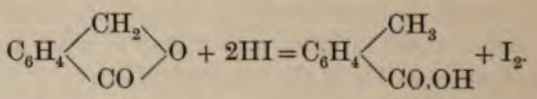
[4] Meister, Lucius and Brüning, *Ber. Deutsch. Chem. Ges.* xvi. 817; Bornemann, *loc. cit.*

[5] *Ann. Chem. Pharm.* cxxiv 254.

THE TOLUIC ACIDS, $C_6H_4\Big\langle\begin{matrix}CH_3\\CO_2H\end{matrix}$.



2222 *Orthotoluic acid* was first obtained by Bieber and Fittig by oxidizing orthoxylene with dilute nitric acid.[1] It may also be easily prepared from its nitril, and its ethyl ether is formed by the action of ethyl chlorocarbonate on a mixture of ortho-iodotoluene and sodium amalgam.[2] It is best prepared by heating phthalide with phosphorus and hydriodic acid:[3]



$$C_6H_4\Big\langle\begin{matrix}CH_2\\CO\end{matrix}\Big\rangle O + 2HI = C_6H_4\Big\langle\begin{matrix}CH_3\\CO.OH\end{matrix} + I_2.$$

It crystallizes in long, lustrous needles, which melt at 102°, and are slightly soluble in cold, more readily in hot water and very readily in alcohol.

It is completely burnt by chromic acid solution, while dilute nitric acid[4] and alkaline permanganate[5] convert it into phthalic acid.

Calcium orthotoluate, $(C_8H_7O_2)_2Ca + 2H_2O$, crystallizes in small needles, which are readily soluble in water but only slightly in alcohol.

Ethyl orthotoluate, $C_8H_7O_2.C_2H_5$, is a liquid which boils at 219·5°, and has an aromatic odour.[6]

Orthotoluyl chloride, $CH_3.C_6H_4.COCl$, is a liquid which boils at 211° (Ador and Rilliet).

Orthotoluamide, $CH_3.C_6H_4.CONH_2$, crystallizes from boiling water in fine, silky needles, melting at 138°.

Orthotolunitril, $CH_3.C_6H_4.CN$, is formed by the distillation of potassium orthoxylenesulphonate with potassium cyanide,[7] and also when orthotolyl mustard oil is heated for an hour with copper filings.[8] It is a colourless, strongly refractive liquid boiling at 203°—204°, which is converted into the amide by heating with alcoholic potash, and into the acid by concentrated hydrochloric acid at 180°—200°.

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[1] *Ann. Chem. Pharm.* clvi. 242.

[2] Kekulé, *Ber. Deutsch. Chem. Ges.* vii. 1007.

[3] Gräbe, *ibid.* xix. 778.

[4] Weith, *ibid.* vii. 1057.

[5] Piccard, *ibid.* xii. 579.

[6] Ador and Rilliet, *ibid.* xii. 2298.

[7] Fittig and Ramsay, *Ann. Chem. Pharm.* clxviii. 246.

[8] Weith, *Ber. Deutsch. Chem. Ges.* vi. 418.

Chlororthotoluic acids, $C_6H_3Cl(CH_3)CO_2H$, are obtained by oxidizing the chloroxylenes with dilute nitric acid:[1]

Cl	CH_3	CO_2H		Melting-point.
4	2	1	compact prisms	130°
4	1	2	compact prisms	166°
3	2	1	needles	154°

a-Bromorthotoluic acid, $C_6H_3Br(CH_3)CO_2H$ (4 : 1 : 2), is formed by the oxidation of bromorthoxylene, and crystallizes from hot alcohol in stellate aggregates of flat needles, which melt at 174°—176°.[2]

β-Bromorthotoluic acid (3 : 1 : 2) is obtained by the action of bromine on orthotoluic acid. It is scarcely soluble in cold, slightly in boiling water, but readily in alcohol, and crystallizes in long needles, melting at 167°.[3]

Nitro-orthotoluic acids, $C_6H_3(NO_2)(CH_3)CO_2H$. The first of these is formed, together with the second, by the nitration of orthotoluic acid,[4] and, together with the third, when nitro-orthoxylene is oxidized.[5] The last also occurs, according to Racine, in the products of the nitration of orthotoluic acid.[6]

	NO_2	CH_3	CO_2H		Melting-point.
a)	4	1	2	needles or microscopic prisms	179°
β)	6	1	2	needles	145°
γ)	4	2	1	long, lustrous needles	152°

Amido-orthotoluic acids, $C_6H_3(NH_2)(CH_3)CO_2H$:

	NH_2	CH_3	CO_2H		
a)	4	1	2	small prisms	196°
β)	6	1	2	small, lustrous needles	191°
γ)	4	2	1	long, flat needles	153°

The last of these acids decomposes into carbon dioxide and metatoluidine when it is heated with lime (Jacobsen).

Sulphorthotoluic acid, $C_6H_3(SO_3H)(CH_3)CO_2H$ (1 : 2 : 3), is obtained by heating orthotoluic acid to 160° with sulphuric acid; it forms a fibrous crystalline mass, which dissolves readily in water, but only slightly in dilute sulphuric acid.

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[1] Krüger, *Ber. Deutsch. Chem. Ges.* xviii. 1755.

[2] Jacobsen, *ibid.* xvii. 2372.

[3] Jacobsen and Wierss, *ibid.* xvi. 1956.

[4] Fittig and Bieber, *Ann. Chem. Pharm.* cxlvi. 245; Fittig and Ramsay, *ibid.* clxviii. 250; Jacobsen and Wierss, *Ber. Deutsch. Chem. Ges.* xvi. 1956.

[5] Jacobsen, *ibid.* xvii. 162.

[6] *Ibid.* xviii. 3450.

Disulphorthotoluic acid, $C_6H_2(SO_3H)_2(CH_3)CO_2H$, is formed when orthotoluic acid is heated to 170° with disulphuric acid; it forms microscopic needles, which are extremely soluble in water (Jacobsen and Wierss).

Parasulphamido-orthotoluic acid, $C_6H_3(SO_2.NH_2)(CH_3)CO_2H$ (4 : 2 : 1), is formed, together with the following compound, when orthoxylenesulphamide is oxidized with an alkaline solution of potassium permanganate. It is slightly soluble in cold, readily in hot water, and crystallizes in long needles, which melt at 217°. Its potassium salt crystallizes in large, compact rhombohedra.

Metasulphamido-orthotoluic acid (4 : 1 : 2) is less soluble in hot water than the isomeric acid, and forms long, brittle needles, melting at 243°. Its potassium salt is extremely soluble, and can only be obtained in a crystalline state by exposing its concentrated solution over sulphuric acid for a long time.[1]

2223 *Metatoluic acid* is obtained by the oxidation of metaxylene with nitric acid[2] or potassium permanganate.[3] Richter prepared it from orthonitrotoluene by converting this into bromometatolunitril by heating with alcohol and potassium cyanide (p. 217), and treating the acid obtained from this with sodium amalgam and water.[4] It has also been obtained from mesitylene, or symmetric trimethylbenzene, by oxidizing this to uvitic acid, $C_6H_3(CH_3)(CO_2H)_2$, and heating the calcium salt of the latter with half its weight of slaked lime to above the melting-point of lead.[5]

In order to prepare it, metaxylene is heated to 130°—150° for one or two days with a mixture of one volume of nitric acid and two volumes of water, and the product distilled with steam, isophthalic acid and nitro-compounds being left behind (Brückner).

Metatoluic acid is more readily soluble in water than its isomerides, and crystallizes, when its solution is rapidly cooled, in long, fine needles, while it is deposited on gradual evaporation in clear, well-formed prisms. It melts at 108°—109°, and readily sublimes.

Calcium metatoluate, $(C_8H_7O_2)_2Ca + 3H_2O$, crystallizes in aggregates of lustrous needles, similar to those of calcium benzoate.

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[1] Jacobsen, *Ber. Deutsch. Chem. Ges.* xiv. 38.

[2] Ahrens, *Zeitschr. Chem.* 1869; 106; Tawildarow, *Ber. Deutsch. Chem. Ges.* iv. 410; Brückner, *ibid.* ix. 405.

[3] Schrötter, *Kekulé's Org. Chem.* iii. 701.

[4] *Ber. Deutsch. Chem. Ges.* v. 424.

[5] Böttinger and Ramsay, *ibid.* ix. 405.

Ethyl metatoluate, $C_8H_7O_2.C_2H_5$, is a liquid, which boils at 224·5°—226·5°.[1]

Metatoluyl chloride boils at 218° (Ador and Rilliet).

Metatolunitril, $C_6H_4(CH_3)CN$, has been obtained by heating metatolyl mustard oil with copper dust as a liquid which smells like benzonitril, and is converted into metatoluic acid by heating with concentrated hydrochloric acid to 180°—200°.[2]

Chlorometatoluic acid, $C_6H_3Cl(CH_3)CO_2H$ (4 : 3 : 1), is formed by boiling a-chlorometaxylene with chromic acid,[3] as well as by replacing the amido-group of amidometatoluic acid by chlorine.[4] It is only very slightly soluble in water, and sublimes in dazzling white needles, which melt at 209°—210°.

a-Bromometatoluic acid, $C_6H_3Br(CH_3)CO_2H$ (4 : 3 : 1), is obtained by the oxidation of bromometaxylene[5] and of *a*-bromo-isocymene,[6] as well as, together with the *β*-acid, by the bromination of metatoluic acid.[7] It separates from hot alcohol as a crystalline powder or in small thick prisms, which melt at 209°—210°.

β-Bromometatoluic acid (4 : 1 : 3) is formed by the oxidation of *β*-bromo-isocymene, and separates from hot glacial acetic acid as a faintly lustrous, crystalline powder, melting at 152°—153°.[8]

Nitrometatoluic acids, $C_6H_3(NO_2)(CH_3)CO_2H$. Two of these are formed by the nitration of metatoluic acid,[9] and both the others by the oxidation of the corresponding nitrometaxylene,[10] while the third has also been obtained by the oxidation of nitro-isocymene:[11]

	NO_2	CH_3	CO_2H		Melting-point.
a)	4 :	1 :	3	compact prisms	219°
β)	2 :	1 :	3	compact prisms	182°
γ)	6 :	1 :	3	lustrous needles or crystalline powder	214°
δ)	5 :	1 :	3	silky needles	167°

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[1] Ador and Rilliet, *Ber. Deutsch. Chem. Ges.* xii. 2300.

[2] Weith and Landolt, *ibid.* viii. 719.

[3] Volrath, *Ann. Chem. Pharm.* cxliv. 266; Jacobsen, *Ber. Deutsch. Chem. Ges.* xviii. 1760.

[4] Beilstein and Krüsler, *Ann. Chem. Pharm.* cxliv. 181.

[5] Fittig, Ahrens and Mattheides, *ibid.* cxlvii. 32.

[6] Kelbe, *Ber. Deutsch. Chem. Ges.* xv. 39.

[7] Jacobsen, *ibid.* xiv. 2351.

[8] Kelbe and Czarnomski, *Ann. Chem. Pharm.* ccxxxv. 291.

[9] Jacobsen, *Ber. Deutsch. Chem. Ges.* xiv. 2353.

[10] Kreusler and Beilstein, *loc. cit.*; Remsen and Kuhara, *Amer. Chem. Journ.* iii. 424; Thöl, *Ber. Deutsch. Chem. Ges.* xviii. 359.

[11] Kelbe and Warth, *Ann. Chem. Pharm.* ccxxi. 161.

Amidometatoluic acids, $C_6H_3(NH_2)(CH_3)CO_2H$, have been prepared by the reduction of the first three nitro-acids with tin and hydrochloric acid:

	NH_2	CH_3	CO_2H		Melting-point.
α)	4	1	3	long, thin, colourless plates .	172°
β)	2	1	3	small, flat prisms	132°
γ)	6	1	3	long needles	167°

a-Sulphamidometatoluic acid, $C_6H_3(SO_2.NH_2)(CH_3)CO_2H$ (4 : 3 : 1), is formed when a-metaxylenesulphamide is oxidized with chromic acid or potassium permanganate; it crystallizes from hot water in long needles, melting at 254°.[1]

v-Sulphamidometatoluic acid (2 : 3 : 1) has been obtained by the oxidation of v-metaxylenesulphamide, and forms crystals which melt at 202°—203° (Jacobsen).

2224 *Paratoluic acid* was prepared by Noad in 1847 by the oxidation of cymene, $CH_3.C_6H_4.C_3H_7$, with nitric acid;[2] it is formed in this way from many other hydrocarbons which contain two side-chains in the para-position, such as paramethylethylbenzene,[3] paraxylene,[4] &c. The latter is also converted into the acid by the action of potassium permanganate[5] and of chromyl chloride.[6] Oil of turpentine and its isomerides, which must be looked upon as dihydroxycymenes, and various derivatives of these are also oxidized to paratoluic acid by dilute nitric acid.[7] Kekulé obtained it synthetically by the action of carbon dioxide on a mixture of sodium and parabromotoluene,[8] while Wurtz obtained the ethyl ether by employing ethyl chloro-carbonate.[9] It has also been synthetically prepared by many of the reactions previously mentioned (Part III., p. 30).

The cymene which is contained in Roman cumin oil and which can easily be obtained from camphor, is employed as the starting point in the preparation of the acid. It is heated for a considerable time in an apparatus connected with an inverted condenser with a mixture of 1 vol. of nitric acid of spec. gr. 1·38 and 4 vols. of water, then neutralized with caustic soda and boiled in order to remove unattacked cymene and nitro-products. It is then precipitated with hydrochloric acid and the precipitate freed from nitroparatoluic acid, &c., by boiling with tin and hydrochloric acid. The product always contains terephthalic acid, which remains behind on treatment with water. The paratoluic acid is finally purified by distillation with steam.[1]

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[1] Iles and Remsen, *Ber. Deutsch. Chem. Ges.* x. 1044; xi. 229 and [illegible]88; Jacobsen, *ibid.* xi. 895; Coale and Remsen, *Amer. Chem. Journ.* iii. 205.

[2] *Chem. Soc. Mem.* iii. 425.

[3] Jannasch and Dieckmann, *Ber. Deutsch. Chem. Ges.* vii. 1514.

[4] Yssel de Schepper and Beilstein, *Ann. Chem. Pharm.* cxxxvii. 306.

[5] Berthelot, *Bull. Soc. Chim.* vii. 134.

[6] Carstanjen, *Ber. Deutsch. Chem. Ges.* ii. 635.

[7] Hirzel, *Zeitschr. Chem.* 1866, 205; Mielk, *Ann. Chem. Pharm.* clxxx. [illegible]9; Hempel, *ibid.* clxxx. 74; Köbig, *ibid.* cxcv. 106.

[8] *Ibid.* cxxxvii. 184.

[9] *Ibid.* Suppl. vii. 127.

It crystallizes in needles, which are slightly soluble in cold, more readily in hot water, and very readily in alcohol and ether; it melts at 180°, boils at 274°—275°,[2] and is readily volatile with steam. It is converted into terephthalic acid by oxidation.

All its salts are soluble in water.

Calcium paratoluate, $(C_8H_7O_2)_2Ca + 3H_2O$, crystallizes from hot water in dazzling white needles, which resemble those of calcium benzoate.

Methyl paratoluate, $C_8H_7O_2.CH_3$, forms crystals which have a very pleasant, penetrating odour; it melts at 32° and boils at 217° (Fischli).

Ethyl paratoluate, $C_8H_7O_2.C_2H_5$, is a liquid, which boils at 228°, has a bitter taste and a smell resembling that of ethyl benzoate (Noad).

Phenyl paratoluate, $C_8H_7O_2.C_6H_5$. When paratoluyl chloride is heated with sodium salicylate, a viscid mass of paratoluyl-salicylic acid, $CH_3.C_6H_4CO.OC_6H_4.CO_2H$, resembling turpentine, is formed and decomposes into phenyl paratoluate and carbon dioxide on distillation with lime. It forms white plates, which have a nacreous lustre, smell like the geranium and melt at 71°—72°.[3]

Paratoluyl chloride, $CH_3.C_6H_4.COCl$, is a strongly refractive liquid, boiling at 218°.[4]

Paratoluamide, $CH_3C_6H_4.CO.NH_2$, crystallizes from hot water in needles or plates, which melt at 151° (Fischli).

Paratoluylamido-acetic acid, $CH_3.C_6H_4.CO.NH.CH_2.CO_2H$, which is also called *toluric acid*, occurs in the urine after the administration of paratoluic acid. It is slightly soluble in cold, readily in hot water and alcohol, and crystallizes in nacreous plates or rhombic tablets, which melt at 160°—165°, and are decomposed into paratoluic acid and amido-acetic acid by continued boiling with hydrochloric acid.[1]

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[1] Dittmar and Kekulé, *Ann. Chem. Pharm.* clxii. 339; Brückner, *ibid.* ccv. 113.

[2] Fischli, *Ber. Deutsch. Chem. Ges.* xii. 615.

[3] Kraut, *Chem. Centralbl.* 1859, 84.

[4] Cahours, *Ann. Chem. Pharm.* cviii. 316; Brückner, *ibid.* ccv. 114; Ador and Rilliet, *Ber. Deutsch. Chem. Ges.* xii. 2298.

Schultzen and Naunyn, after taking coal-tar xylene, found in the urine a toluric acid, which did not crystallize but was only obtained as a colourless liquid;[2] this substance probably consists entirely or chiefly of the meta-compound.

Paratolunitril, $CH_3.C_6H_4.CN$, is best prepared by distilling paratoluic acid with potassium thiocyanate (Part III., p. 19[illegible]). It is a powerfully refractive liquid, smelling like benzonitril, boils at 217·8° and solidifies at a low temperature to a mass, which melts at 28·5°.[3]

Chloroparatoluic acid, $C_6H_3Cl(CH_3)CO_2H$ (3 : 4 : 1), is formed by the oxidation of chlorocymene, $C_6H_3Cl(CH_3)C_3H_7$, with dilute nitric acid.[4] It is slightly soluble in hot water, readily in alcohol, and crystallizes in large plates melting at 194°—196°.

a-Bromoparatoluic acid, $C_6H_3Br(CH_3)CO_2H$ (3 : 4 : 1), has been obtained by the oxidation of orthobromocymene,[5] bromethylmethylbenzene,[6] and bromoparaxylene,[7] and is also formed when paratoluic acid is allowed to stand in contact with dry bromine.[8] It is almost insoluble in cold, slightly soluble in hot water and readily in alcohol, crystallizing in needles, which melt at 204°.

β-Bromoparatoluic acid, which is formed by the oxidation of metabromocymene, crystallizes from alcohol in plates melting at 196°.[9]

Dibromoparatoluic acid, $C_6H_2Br_2(CH_3)CO_2H$ (3 : 6 : 4 : 1), is obtained by oxidizing solid dibromoparaxylene with a solution of chromium trioxide in acetic acid. It is only very slightly soluble in water, and crystallizes from alcohol in stellate aggregates of needles, which melt at 195°.[10]

Iodoparatoluic acid, $C_6H_3I(CH_3)CO_2H$, was obtained by Griess together with amidoparatoluic acid, by the action of hydriodic acid on diazo-amidotoluic acid, it is slightly soluble in water, readily in alcohol, and crystallizes in white plates or needles.

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[1] Kraut, *Ann. Chem. Pharm.* xcviii. 360.

[2] *Zeitschr. Chem.* 1868, 29.

[3] Paternò and Pisati, *Ber. Deutsch. Chem. Ges.* viii. 441; see also Volra[illegible]th, *Zeitschr. Chem.* 1866, 489; Hofmann, *Ann. Chem. Pharm.* cxlii. 126; M[illegible]rz, *Zeitschr. Chem.* 1868, 33; Weith, *Ber. Deutsch. Chem. Ges.* vi. 421.

[4] Kekulé and Fleischer, *ibid.* vi. 1090; v. Gerichten, *ibid.* x. 1250; xi. 368.

[5] Landolph, *Ber. Deutsch Chem. Ges.* v. 268.

[6] Fittica, *Ann. Chem. Pharm.* clxxii. 312.

[7] Morse and Remsen, *Ber. Deutsch. Chem. Ges.* xi. 225.

[8] Jannasch and Dieckmann, *Ann. Chem. Pharm.* clxxi. 83.

[9] Kelbe and Koschnitzky, *ibid.* xix. 1730.

[10] Schultz, *ibid.* xviii. 1762.

α-Nitroparatoluic acid, $C_6H_3(NO_2)(CH_3)CO_2H$ (3 : 4 : 1), is formed by the action of fuming nitric acid on cymene[1] or paratoluic acid.[2] It is slightly soluble in cold, more readily in hot water and readily in alcohol, from which it crystallizes in light yellow, monoclinic prisms, which melt at 189°—190°.

β-Nitroparatoluic acid (2 : 4 : 1) is obtained by the oxidation of liquid nitrocymene with chromic acid solution (Landolph, Fittica). It is scarcely soluble in cold, slightly in hot water, and only with difficulty in alcohol, crystallizing in small plates or needles, which sublime without melting when heated. According to Widman and Bladin, the so-called liquid nitrocymene consists chiefly of paratolylmethylketone,[3] and the acid prepared from it is therefore probably not a nitrotoluic acid.

β-Nitroparatolunitril, $C_6H_3(NO_2)(CH_3)CN$, is obtained by heating the diazo-compound of metanitroparatoluidine with potassium cuprocyanide; it melts at 99°—100°.[4]

α-Amidoparatoluic acid, $C_6H_3(NH_2)(CH_3)CO_2H$ (3 : 4 : 1), is tolerably soluble in water and crystallizes in hair-like needles, which melt at 164°—165° (Ahrens).

Diazo-amidotoluicacid, $CO_2H.C_6H_3(CH_3)NH.N{=}NC_6H_3(CH_3)CO_2H$, is formed by the action of nitrogen trioxide on an alcoholic solution of the amido-acid. It forms yellow microscopic prisms, which are insoluble in water and alcohol, and is decomposed by the haloid acids with formation of substituted toluic acids.[5]

Sulphoparatoluic acid, $C_6H_3(SO_3H)(CH_3)CO_2H$ (2 : 1 : 4), has been prepared by the action of sulphur trioxide on paratoluic acid,[6] and by the oxidation of thiocymene, $C_6H_3(SH)(CH_3)C_3H_7$ [7] and cymene-orthosulphonic acid.[8] It crystallizes in small plates which contain two molecules of water and are stable in the air.

Sulphamidoparatoluic acid, $C_6H_3(SO_2.NH_2)(CH_3)CO_2H$, is formed by the oxidation of paraxylenesulphamide[9] or cymene-sulphamide,[10] and crystallizes from hot water in long needles which melt at 167°.[11]

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[1] Noad, *Chem. Soc. Mem.* iii. 431; Ahrens, *Zeitschr. Chem.* 1869, 102; Landolph, *Ber. Deutsch. Chem. Ges.* vi. 936; Fittica, *ibid.* vi. 938.

[2] *Ann. Chem. Pharm.* clxviii. 250.

[3] *Ber. Deutsch. Chem. Ges.* xix. 584.

[4] Leukart, *ibid.* xix. 417.

[5] Griess, *Ann. Chem. Pharm.* cxvii. 58.

[6] Fischli, *Ber. Deutsch. Chem. Ges.* xii. 615.

[7] Flesch, *ibid.* vi. 478; Bechler, *Journ. Prakt. Chem.* [2] viii. 170.

[8] Remsen and Burney, *Amer. Chem. Journ.* ii. 405; Baur and Meyer, *Ann. Chem. Pharm.* ccxx. 18.

[9] Ahrens, *Zeitschr. Chem.* 1869, 102; Landolph, *Ber. Deutsch. Chem. Ges.* vi. 936; Fittica, *ibid.* vi. 938.

[10] *Ann. Chem. Pharm.* clxviii. 250.

[11] Iles and Remsen, *Ber. Deutsch. Chem. Ges.* xi. 230; Hall and Remsen, *ibid.* xii. 1433.

HYDROXYTOLUALDEHYDES, $C_6H_4(OH)(CH_3)COH$.

2225 These compounds are formed when the cresols are heated with caustic soda solution and chloroform, homosalicylaldehydes being formed, which are volatile with steam. Ortho- and meta-cresol also yield homologues of parahydroxybenzaldehyde, which are not volatile with steam, but this is not the case with paracresol, since in the chloroform reaction the aldehyde-group always takes up either the ortho- or para-position with respect to the hydroxyl.[1]

Parahomosalicylaldehyde or *Orthohydroxymetatolualdehyde* ($COH:OH:CH_3 = 1:2:5$) is slightly soluble in water, readily in alcohol, and crystallizes from dilute alcohol in six-sided plates which have a nacreous lustre, and melt at 56°. It boils at 217°—218°, has a powerful, almost repulsive aromatic odour, and gives a deep blue colouration with ferric chloride.

It is converted by the action of water and sodium amalgam into *homosaligenin* or *orthohydroxymetaxylyl alcohol*, $C_6H_3(OH)(CH_3)CH_2.OH$, which crystallizes from hot water in lustrous plates, melts at 105° and, like saligenin, gives a deep blue colouration with ferric chloride.

Orthohomosalicylaldehyde or *Orthohydroxymetatolualdehyde* ($1:2:3$) is an oily liquid, which has a smell resembling both salicylaldehyde and oil of bitter almonds, solidifies on cooling to crystals which melt at 17°, and gives a bluish colouration with ferric chloride.

Metahomosalicylaldehyde or *Orthohydroxyparatolualdehyde* ($1:2:4$) forms crystals, which melt at 54° and have a pleasant aromatic odour. It boils at 222°—223° and gives a violet colouration with ferric chloride,

Orthohomoparahydroxybenzaldehyde or *Parahydroxymetatolualdehyde* ($1:4:3$) crystallizes from hot water in pointed prisms, which occur chiefly in twinned forms, resembling gypsum. It melts at 115° and gives a bluish violet colouration with ferric chloride.

Metahomoparahydroxybenzaldehyde or *Parahydroxyorthotolualdehyde* ($1:4:2$) crystallizes in lustrous plates, melts at 110° and gives a light rose-red colouration with ferric chloride.

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[1] Tiemann and Schotten, *Ber. Deutsch. Chem. Ges.* xi. 770.

Menyanthol, C_8H_8O. An amorphous substance, called *menyanthin*, $C_{30}H_{46}O_{14}$, which has an intensely bitter taste, occurs in the common buckbean (*Menyanthes trifoliata*) and is decomposed by heating with dilute sulphuric acid into grape sugar and menyanthol. This substance is a liquid which smells like benzaldehyde, reduces ammoniacal silver solution, and is converted into a crystalline acid on exposure to the air or on fusion with caustic potash.[1] It is probably identical with orthohomosalicylaldehyde.

HYDROXYTOLUIC ACIDS, $C_6H_3(OH)(CH_3)CO_2H$.

2226 Kolbe and Lautemann, after finding that salicylic acid is formed by the action of carbon dioxide on a mixture of phenol and sodium, prepared its homologue, *cresotic acid*, from the cresol which boils at 120°.[2] The three cresotic acids were then prepared from the isomeric cresols,[3] and, on account of their similarity to salicylic acid, were also called *homosalicylic acids*. Ihle has shown that, like their lower homologue, they may be obtained by passing carbon dioxide over the heated sodium cresols.[4]

These compounds and the other hydroxytoluic acids, the ten of which are all known, are also formed by reactions similar to those employed for the preparation of the hydroxybenzoic acids and other hydroxy-acids (Part III., p. 32).

The dimethyl ethers, $C_6H_3(CH_3)(OCH_3)CO_2.CH_3$, are formed by heating the acids with caustic potash and methyl iodide, and these are converted by saponification into the methoxytoluic acids, $C_6H_3(CH_3)(OCH_3)CO_2H$.[5]

The numbers appended in brackets give the position of the side chains in the order $CO_2H : OH : CH_3$.

Parahomosalicylic acid, *a-Cresotic acid* or *a-Orthohydroxymetatoluic acid* (1 : 2 : 5), may be obtained, in addition to the methods just described, by fusing β-metaxylenol[6] or β-bromometatoluic acid[7] with caustic potash, by the action of nitrous acid on the amidometatoluic acid which melts at 172°,[1] and by heating par cresol with caustic soda and tetrachloromethane.[2] It crystalliz from hot water in very long needles or rhombic prisms, meltin at 151°, and is readily volatile with steam. Its aqueous solutio is coloured an intense violet-blue by ferric chloride; it decomposes into paracresol and carbon dioxide when heated to 18 with hydrochloric acid, while a remarkable reaction occurs whe its calcium salt is heated with lime, orthocresol being forme (Jacobsen).

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[1] Kromayer, *Jahresb. Chem.* 1861, 749.

[2] *Ann. Chem. Pharm.* cxv. 203.

[3] Engelhardt and Latschinow, *Zeitschr. Chem.* 1869, 622; Biedermann, *Ber. Deutsch. Chem. Ges.* vi. 325; Kekulé, *ibid.* vii. 1006.

[4] *Journ. Prakt. Chem.* [2] xiv. 454.

[5] Schall, *Ber. Deutsch. Chem. Ges.* xii. 822.

[6] Jacobsen, *ibid.* xi. 374.

[7] *Ibid.* xiv. 2347.

Methylparahomosalicylic acid forms long, thin needles, melting at 67°.

Orthohomosalicylic acid, *β-Cresotic acid*, or *v-Orthohydroxymetatoluic acid* (1 : 2 : 3) is also formed by fusing v-sulphamidometatoluic acid with caustic potash[3] and by the action of nitrous acid on the amidometatoluic acid melting at 132° (Jacobsen). It crystallizes from hot water in long, flat needles, which melt at 163°—164°. It decomposes into orthocresol and carbon dioxide when heated with hydrochloric acid to 210°; ferric chloride colours its aqueous solution deep violet.

Methylorthohomosalicylic acid crystallizes in feathery needles and melts at 81°.

a-Metahomosalicylic acid, *γ-Cresotic acid*, or *Orthohydroxyparatoluic acid* (1 : 2 : 4) is also obtained by fusing paraxylenol with caustic potash (Jacobsen), and, together with metahomoparahydroxybenzoic acid, when metacresol is heated with tetrachloromethane and caustic soda (Schall). It crystallizes from water in needles and from alcohol in monoclinic prisms, which melt at 177°,[4] and are volatile with steam. On heating with hydrochloric acid to 170°, it decomposes into metacresol and carbon dioxide; ferric chloride produces a deep violet colouration in its aqueous solution.

a-Methylmetahomosalicylic acid crystallizes in plates, which melt at 103°—104°.

β-Metahomosalicylic acid (1 : 2 : 6) has been obtained from β-bromorthotoluic acid. It is slightly soluble in cold, readily in hot water, very freely in alcohol, crystallizes in long needles, melting at 168°, and is tolerably volatile with steam. Its solution is coloured a deep blue-violet by ferric chloride;

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[1] *Ber. Deutsch. Chem. Ges.* xiv. 2352.; Panaotović, *Journ. Prakt. Chem.* [2] xxxiii. 63.

[2] Schall, *ibid.* xii. 821.

[3] *Ber. Deutsch. Chem. Ges.* xi. 902.

[4] Oppenheimer and Pfaff, *ibid.* viii. 889.

on heating to 200° with concentrated hydrochloric acid, it decomposes into metacresol and carbon dioxide.[1]

2227 *Parahomometahydroxybenzoic acid* or *Metahydroxyorthotoluic acid* (1 : 5 : 2) is formed by fusing metasulphamido-orthotoluic acid,[2] α-bromorthotoluic acid,[3] or the chlororthotoluic acid melting at 166°,[4] with caustic potash, and from β-amidorthotoluic acid by means of the diazo-reaction.[5] It is slightly soluble in cold, readily in hot water, crystallizes in transparent prisms, which melt at 172° and sublime in needles, and is also volatile with steam. Ferric chloride, added to its cold saturated solution or to that of its ammonium salt, produces a light brown precipitate soluble in a large quantity of hot water. It is not attacked by concentrated hydrochloric acid even at 220°.

Metahomometahydroxybenzoic acid or *s-Hydroxytoluic acid* (1 : 3 : 5). Fuming sulphuric acid converts metatoluic acid into two isomeric sulphonic acids, which yield a mixture of symmetric hydroxymetatoluic acid and parahomosalicylic acid on fusion with caustic potash; the latter may be removed by distillation with steam, while the former differs from all its isomerides in not being volatile.

Symmetric hydroxytoluic acid is tolerably soluble in cold, readily in hot water, and crystallizes in fascicular aggregates of needles, which melt at 208°; it solidifies to hard, transparent prisms and sublimes in stellate groups of needles. Solutions of the acid and of its salts give a fawn-coloured precipitate with ferric chloride, which dissolves in a large excess of the reagent, forming a dark brown solution. It is not attacked by concentrated hydrochloric acid at 230°, and yields metacresol when distilled with lime.[6]

s-Trinitrohydroxytoluic acid, $C_6(NO_2)_3(OH)(CH_3)CO_2H + H_2O$ Warren de la Rue, by heating the colouring matter of cochineal with nitric acid, obtained *nitrococcusic acid*, which possesses the same composition as the trinitro-anisic acid prepared by Cahours, but is obviously not identical with it.[7] Gmelin states that it is isomeric with the latter and also with methyltrinitrosalicylic acid.[8] It differs from both of these by being dibasic, and Strecker on this account suggested that it might be trinitrocresotic acid.[9]

[1] Jacobsen, *Ber. Deutsch. Chem. Ges.* xvi. 1962.

[2] *Ibid.* xiv. 38.

[3] *Ibid.* xvii. 2375.

[4] Krüger, *ibid.* xviii. 1758.

[5] Jacobsen and Wierss, *ibid.* xvi. 1959.

[6] Jacobsen, *ibid.* xiv. 2357.

[7] *Ann. Chem. Pharm.* lxiv. 23.

[8] *Handb. Org. Chem.* iii. 398.

[9] *Lehrb. Org. Chem.* v. Aufl. 727.

with tetrachloromethane and concentrated caustic soda solution,[1] and when parasulphamido-orthotoluic acid[2] or the chlororthotoluic acid which melts at 130°[3] is fused with caustic potash. It crystallizes from hot water in small needles which contain half a molecule of water of crystallization; this is lost at 100° and the anhydrous residue then melts at 177°—178°. Ferric chloride produces no colouration, but gives a reddish brown precipitate with its salts, which dissolves in an excess of the reagent forming a dark-brown solution. On heating to 200° with hydrochloric acid it decomposes into carbon dioxide and metacresol.

Methylmetahomoparahydroxybenzoic acid crystallizes in long needles and melts at 176°.

Orthohomoparahydroxybenzoic acid or *Parahydroxymetatoluic acid* (1 : 4 : 3) is formed by fusing the aldehyde,[4] a-sulphamidotoluic acid[5] *a*-bromometatoluic acid,[6] or chlorometatoluic acid[7] with caustic potash, and together with a small quantity of orthohomosalicylic acid by heating orthocresol with tetrachloromethane and caustic soda (Schall). It crystallizes from hot water in small needles, containing half a molecule of water, which is lost at 100°; the anhydrous acid melts at 171°—173°, and is volatile with steam. Ferric chloride produces no colouration; on heating with hydrochloric acid to 180°—185° it decomposes into carbon dioxide and orthocresol.

Methylorthohomoparahydroxybenzoic acid forms microscopic silky needles, melting at 192°—193°.

DIHYDROXYTOLUALDEHYDES,

$C_6H_2(CH_3)(OH)_2CHO$.

2229 *Para-orsellinaldehyde*,(CHO : OH : OH : CH_3 = 1 : 2 : 4 : 6). This compound, which is also known as *orcylaldehyde*, is formed together with two orcendialdehydes, $C_6H(CH_3)(OH)_2(CHO)_2$, by heating orcinol with caustic potash and chloroform; it crystallizes from hot water in fascicular or stellate aggregates of needles, which melt at 177°—178°. Its aqueous solution is coloured reddish brown by ferric chloride.[8] The constitution of this body has not been determined, but since resorcinol is converted by the above reaction into β-resorcylaldehyde, in which the aldehyde group takes the para-position with regard to one hydroxyl and the ortho-position to the other, this is probably also the case with orcylaldehyde.

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[1] Schall, *Ber. Deutsch. Chem. Ges.* xii. 819.

[2] Jacobsen, *ibid.* xiv. 40.

[3] Krüger, *loc. cit.*

[4] Schotten and Tiemann.

[5] Jacobsen, *ibid.* xi. 897.

[6] Jacobsen, *ibid.* xiv. 2351.

[7] *Ibid.* xviii. 1760.

[8] Tiemann and Helkenberg, *ibid.* xii. 999.

Metahomomethoxysalicylaldehyde (1 : 2 : 3 : 5) has been obtained from creosol and chloroform, and forms an oily liquid, which possesses a smell resembling that of salicylaldehyde, and, like the latter, forms a deep yellow coloured solution in alkalis. Ferric chloride produces a deep green colouration.[1]

DIHYDROXYTOLUIC ACIDS, $CH_3.C_6H_2(OH)_2CO_2H$.

2230 In the year 1830, Heeren investigated the lichens *Rocella tinctoria* and *Lecanora tartarea*, which are employed in Holland for the manufacture of litmus and archil, and found in them a characteristic, colourless, crystalline substance, which is converted into a red dye by the united action of air and ammonia, and which he therefore named *erythrin* (ἐρυθρός, red). On boiling with a solution of ammonium carbonate, it was converted into the amorphous *erythrinbitter*. In order to obtain erythrin in larger quantities, he extracted the lichens with alcohol, but found that the erythrin was thus converted into a similar substance, which was, however, unsuitable for the preparation of the dye, and which he named *pseudoerythrin*.[2] He also found rocellic acid in the lichens which he examined (Pt. II. p. 289).

Kane, however, obtained different results; in extracting the lichens with hot alcohol he obtained *erythrylin*, insoluble in water, and a soluble crystalline compound, which is identical with pseudoerythrin and is not an accidental product, but one of the most important of the whole series. He therefore transferred the name erythrin to this substance and assumed that Heeren's erythrin was a mixture of erythrylin with other bodies. When its solution is exposed to the air, erythrinbitter or *amarythrin* is formed, and this converted after several months' exposure into crystalline *telerythrin*, to which he gave this name in contradistinction to erythrylin, since the word τέλος denotes the end, and ὕλη the beginning of the series.[3]

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[1] Tiemann and Koppe. *Ber. Deutsch. Chem. Ges.* xiv. 2026.

[2] *Schweigger's Journ.* lix. 313.

[3] *Phil. Trans.* 1840, 273.

Schunck then investigated many varieties of *Lecanora* and *Variolaria* from the Vogelsberg, and found in them a crystalline compound, which, like Heeren's erythrin, is converted into a red dye by exposure to the air, but has a different composition, and which he therefore named *lecanorin*.[1] On boiling with baryta water, it decomposed into carbon dioxide and orcinol, which had already been prepared from these species of lichens by Robiquet, while on boiling with alcohol it was converted into Heeren's pseudoerythrin.[2]

Rochleder and Heldt, who detected lecanorin in *Evernia Prunastri*, showed that it is also converted into pseudoerythrin by the action of hydrochloric acid and alcohol; the latter substance must therefore be looked upon as the ethyl ether of lecanorin, or as it is more suitably called, *lecanoric acid*.[3]

This compound was then carefully examined by Schunck,[4] who also submitted the substances contained in *Rocella tinctoria var. fuciformis* from Madagascar and Angola to a new investigation. The most important of these is erythric acid, which yields the colouring matter. This is so readily converted into the ethyl ether or pseudoerythrin by boiling with alcohol, that the latter is always obtained when the lichens are extracted with boiling alcohol. This compound has the same composition as ethyl-lecanoric acid, and appears to be identical with it—a fact which admits of the simple explanation that erythric acid is a copulated compound of lecanoric acid and orcinol. On boiling with alcohol, orcinol is set free and the lecanoric acid combines with the ethoxyl residue.[5]

Erythric acid is converted by boiling with water into *picroerythrin*, the properties of which are not identical either with those of Heeren's erythrinbitter or of Kane's amarythrin; they approach most closely to those of telerythrin.

Stenhouse, who investigated a South American sample of *Rocella tinctoria*, found in it α-orsellic acid, which is decomposed by boiling with milk of lime or baryta into orcinol and α-orsellinic acid, while Schunck's lichen, which is *R. Montagnei*, contains erythric acid, which yields picroerythrin and *erythrelinic acid*, which is very similar to α-orsellinic acid. According to Schunck, picroerythrin is decomposed by boiling with an excess of lime or baryta into carbon dioxide and orcinol, but Stenhouse has shown that *erythroglucin* is also formed.[1]

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[1] *Ann. Chem. Pharm.* xli. 157.

[2] *Ibid.* xlv. 250.

[3] *Ibid.* xlviii. 1.

[4] *Ibid.* liv. 261.

[5] *Ibid.* lxi. 64.

Stenhouse also discovered a *β-orsellic acid* in *Rocella tinctoria* from the Cape of Good Hope, but this was shown by Gerhardt, who was subsequently confirmed by Stenhouse himself, to be identical with the *a*-acid.

In "Remarks on the Preceding Communication," Strecker observes: Stenhouse has made us acquainted with a series of acids which are of special interest, both on account of their similar properties and analogous reactions, and from the fact of their occurrence in the same plants. It is for this reason desirable that the changes undergone by these compounds should be represented by formulæ, and for this purpose it is necessary to substitute new expressions for some of the empirical formulæ given by Stenhouse, since the former agree equally well with the experimental results and are also capable of representing the decompositions and reactions of the substances in question.

a-Orsellic acid, then, is converted into two molecules of orsellinic acid, the elements of water being taken up:

$$C_{16}H_{14}O_7 + H_2O = 2C_8H_8O_4.$$

The former can also form orcinol with loss of carbon dioxide:

$$C_{16}H_{14}O_7 + H_2O = 2C_7H_8O_4 + 2CO_2.$$

The conversion of orsellinic acid into orcinol takes place with the separation of carbon dioxide:

$$C_8H_8O_4 = C_7H_8O_2 + CO_2.$$

Erythric acid is resolved into picroerythrin and erythrelic acid, which is undoubtedly orsellinic acid:

$$C_{20}H_{22}O_{10} + H_2O = C_{12}H_{16}O_7 + C_8H_8O_4.$$

Finally, picroerythrin decomposes into carbon dioxide, orcinol and erythroglucin:

$$C_{12}H_{16}O_7 + H_2O = CO_2 + C_7H_8O_2 + C_4H_{10}O_4.$$

He adds that erythric acid can yield twice as much orsellinic acid as given by the equation, but Stenhouse considers this as improbable. In this case the formula of the former would be $C_{14}H_{15}O_7$:[2]

$$2C_8H_8O_4 + C_{12}H_8O_7 = 2C_{14}H_{15}O_7 + H_2O.$$

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[1] Stenhouse, *Phil. Trans.* 1848, 63.

[2] *Ann. Chem. Pharm.* lxviii. 108.

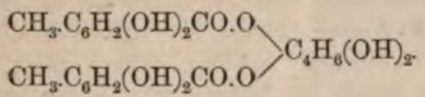
Gerhardt came to the conclusion that orsellic acid has the formula $C_{16}O_{14}O_7$, and is identical with lecanoric acid,[1] while Schunck expressed the opinion that the ethyl ether of orsellinic acid is identical with that of lecanoric acid, just as is the case with erythrin and pseudoerythrin.[2]

Hesse then undertook a new investigation of these lichen substances. He ascertained that the Angola lichen, which comes into the market under many names, is *Rocella fuciformis*, and retained Heeren's name of erythrin for the chromogen contained in it, since it scarcely possesses the properties of an acid. His analysis gave him results in accordance with Strecker's second formula, which, however, he doubled and wrote $C_{28}H_{30}O_{14}$. The acid obtained from it by decomposition proved as Strecker had correctly foreseen, to be identical with orsellinic acid.[3]

Stenhouse confirmed these observations, and adopted the same formula for erythrin, giving equations to explain its changes and decompositions,[4] but, in spite of this, Strecker's first formula has been shown to be correct.

After it had been recognized that erythroglucin or erythrol as it is now called, is an alcohol, Berthelot suggested that erythrin is the orsellinic ether of this, and de Luynes has observed that it is in fact the di-acid ether of this alcohol, picroerythrin being the mono-acid derivative.[5] Orsellinic acid has proved to be a dihydroxytoluic acid, and the compounds in question have, therefore, the following constitution :

Erythrin :



$$\left.\begin{array}{l}CH_3.C_6H_2(OH)_2CO.O\\CH_3.C_6H_2(OH)_2CO.O\end{array}\right>C_4H_6(OH)_2.$$

Picroerythrin :

$$CH_3.C_6H_2(OH)_2CO.OC_4H_6(OH)_3.$$

Further investigations conducted by Hesse have finally decided that the archil lichens which occur in commerce consist chiefly of two species. *Rocella fuciformis* (Acharius) comprises those from Lima, Angola, Mozambique, Zanzibar and Ceylon; this contains erythrin alone, while *Rocella tinctoria* (De Candolle), which comes from Cape Verde and the neighbouring islands, contains a chromogen, lecanoric acid,[1] which is identical with orsellic acid.

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[1] *Compt. Rend. Chim.* 1849, 127.

[2] *Phil. Mag.* xxxiii. 249.

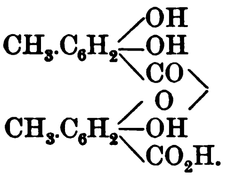
[3] *Ann. Chem. Pharm.* cxvii. 297.

[4] *Proc. Roy. Soc.* xii. 263.

[5] *Ann. Chem. Pharm.* cxxxii. 355.

Stenhouse remarks on this point that the South American lichens examined by him are also *Rocella tinctoria.* They are sent into the market under the name of Valparaiso lichens, but are seldom exported to England, while the Lima lichens (*Rocella fuciformis*) are sent there in large quantities.[2]

Lecanoric acid is monobasic and stands in the same relation to orsellic acid as glycollic acid to glycoglycollic acid :



2231 *Orsellinic acid*, $CH_3.C_6H_2(OH)_2CO_2H+H_2O$, is readily prepared from erythrin by heating it on the water bath with baryta water until barium carbonate commences to separate. A few drops of the solution are then tested with hydrochloric acid at short intervals, and as soon as a gelatinous precipitate is no longer formed, hydrochloric acid is added to the solution, the orsellinic acid being thus soon precipitated. It crystallizes from acetic acid in stellate aggregates of needles, and separates from dilute alcohol as a crystalline mass, which is readily soluble in water, becomes anhydrous at 100°, and melts at 176°, a gradual decomposition into carbon dioxide and orcinol accompanied by violent frothing, taking place. The same decomposition occurs on boiling with water or alkalis. Its aqueous solution is coloured purple-violet by ferric chloride, and gives an amorphous precipitate with an ammoniacal solution of lead acetate.

Barium orsellinate, $(C_8H_7O_4)_2Ba$, is extremely soluble in water, and crystallizes from dilute alcohol in hydrated prisms, which decompose even at 100° with formation of barium carbonate.

Methyl orsellinate, $C_8H_7O_4(CH_3)$, is formed by boiling lecanoric acid (Schunck) or erythrin (Stenhouse) with methyl alcohol, and crystallizes in lustrous needles, or flat, pointed prisms, which are readily soluble in water. It dissolves in alkalis and is reprecipitated by acids.

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[1] *Ann. Chem. Pharm* cxxxix. 22.

[2] *Journ. Chem. Soc.* v. 221.

Ethyl orsellinate, $C_8H_7O_4(C_2H_5)$. The formation of this ether, which was described by Heeren as pseudoerythrin, has been frequently referred to in the preceding pages. It is slightly soluble in cold, readily in hot water and alcohol, and crystallizes in needles or small plates, which melt at 132°. Its aqueous solution is precipitated by lead acetate.

Amyl orsellinate, $C_8H_7O_4(C_5H_{11})$, is prepared by boiling erythrin with amyl alcohol. It is scarcely soluble in water, readily in alcohol and ether, from which it crystallizes in vitreous prisms, melting at 76°.[1]

Orsellinic acid is decomposed by the action of bromine into carbon dioxide and tribromorcinol; if, however, the substances are mixed in ethereal solution, substitution products are formed.

Dibromorsellinic acid, $C_8H_6Br_2O_4$, is slightly soluble in hot water, readily in alcohol and ether, and crystallizes in small, white prisms; its alcoholic solution is coloured a splendid dark blue by ferric chloride, and blood-red by bleaching powder (Hesse).

Phosphorsellinic acid, $C_{40}H_{36}P_4O_{24}$. When orsellinic acid is gradually heated with phosphorus oxychloride to 90°—100°, the liquid becomes coloured brown, violet-green, and, finally, indigo-blue. If it be now allowed to drop into ice water, phosphorsellinic acid separates out, and may be purified by repeated solution in water and precipitation with hydrochloric acid or common salt. It is an amorphous, indigo-blue powder, which takes a cupreous lustre under strong pressure and readily forms deep blue solutions in water and alcohol. The solution in 20,000 parts of water has the colour of a concentrated solution of copper sulphate and a distinct violet colouration is visible when 50,000 parts of water are employed. It dissolves in alkalis, lime water and baryta water with a violet-red colour; the salts of the heavy metals produce bluish violet, flocculent precipitates.

Phosphorsellinanilide, $C_{40}H_{34}(C_6H_5.NH)_2P_4O_{22}$, is formed by boiling the acid with aniline and alcohol; it is a dark violet powder, which is insoluble in water, but forms a splendid violet solution in alcohol.[2]

2232 *Lecanoric acid* or *Diorsellinic acid*, $C_{16}H_{14}O_7 + H_2O$, is, according to Hesse, best prepared from the *R. tinctoria* from Cape Verde. The lichens are extracted with ether, and the greenish white, crystalline residue left after the evaporation of the ether dissolved in milk of lime, filtered, precipitated with sulphuric acid and crystallized from alcohol. It is scarcely soluble in cold water, but dissolves in 2,500 parts of boiling water, more readily in alcohol and ether, and crystallizes in needles or prisms, which become anhydrous at 100°, melt at 153°, and simultaneously decompose with evolution of carbon dioxide. The alcoholic solution is coloured dark purple-red by ferric chloride and is not precipitated by lead acetate; copper acetate, however, produces a pale, apple-green precipitate on standing (Schunck). It reduces ammoniacal silver solution on heating, and is converted on boiling with water into orsellinic acid, and with alcohol into its ether.

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[1] Hesse, *Ann. Chem. Pharm.* cxxxix. 22.

[2] Schiff, *ibid.* ccxxviii. 56.

Barium lecanorate, $(C_{16}H_{13}O_7)_2Ba$, separates from hot alcohol in small, star-shaped aggregates of needles.

Substitution products are formed by the action of bromine on an ethereal solution:

	Melting-point
Dibromolecanoric acid, $C_{16}H_{12}Br_2O_7$, small white prisms .	179°
Tetrabromolecanoric acid, $C_{16}H_{10}Br_4O_7$, pale yellow prisms	157°

Both these bodies evolve carbon dioxide on fusion; their alcoholic solutions are coloured purple-red by ferric chloride and blood-red by bleaching powder (Hesse).

Erythrin, $2C_{20}H_{22}O_{10} + 3H_2O$. In order to prepare this substance, 1 part of *R. fuciformis* is macerated for twenty minutes with 10 parts of milk of lime containing 1·6 per cent. of lime, filtered and precipitated immediately with hydrochloric acid. The residue is treated a second time with milk of lime, which is then employed for the extraction of a new quantity of lichen. The precipitate is redissolved in milk of lime, the filtrate treated with carbon dioxide and the precipitated mixture of calcium carbonate and erythrin gently warmed with alcohol; hot water is then added to the solution until a permanent turbidity is produced. The erythrin separates on cooling in spherical crystalline masses, which become anhydrous at 100° and melt at 137°. It is slightly soluble in cold water, with difficulty in ether, but readily in alcohol; ferric chloride added to the alcoholic solution produces a purple-violet colouration, which changes on further addition to a brownish red precipitate.

Picroerythrin, $C_{12}H_{16}O_7 + 3H_2O$, is the first product of the decomposition of erythrin by boiling water, alcohols or alkalis, When erythrin is dissolved in milk of lime it decomposes in the course of a day or two with formation of picroerythrin, which is also obtained pure when erythrin is boiled for some hours with amyl alcohol. It crystallizes in silky prisms, which readily effloresce, melt at 158° and have a slightly sweet and intensely bitter taste. It is exceptionally soluble in hot water and undergoes no change when boiled with absolute alcohol. Ferric chloride produces a purple-violet colouration.

2233 In connection with these compounds, the following, which are to some extent homologous with them, may be mentioned here.

Evernic acid, $C_{17}H_{16}O_7$. According to Rochleder and Heldt, lecanoric acid occurs in *Evernia Prunastri;* Stenhouse, however, could not detect it in lichens grown in Scotland, but found in them evernic acid, together with usnic acid, $C_{18}H_{18}O_7$, thus proving either that the German and Scotch lichens contain different compounds, or, what is much more probable, that the German chemists had not investigated the true *Evernia Prunastri*,[1] a view which is supported by the fact that Hesse, who examined this lichen collected in various parts of Germany, always found evernic acid in it.[2]

It is almost insoluble in water, but dissolves easily in alcohol, and crystallizes in spherical aggregates of needles, which melt at 164°.

Everninic acid, $C_9H_{10}O_4$, is formed, together with carbon dioxide and orcinol, when evernic acid is boiled with lime water or baryta water. It is tolerably soluble in hot water, readily in alcohol, and crystallizes in flat, lustrous needles, resembling those of benzoic acid. It melts at 159°, and on further heating emits a penetrating odour and yields a colourless sublimate. Ferric chloride colours the aqueous solution violet.

Barbatic acid, $C_{19}H_{20}O_7$. This substance, which stands in the same relation to homorcinol (p. 402) as evernic acid to orcinol, occurs with usnic acid in *Usnea barbata*. It crystallizes from benzene in long plates, needles, or short prisms, which melt at 168°, and decompose at a higher temperature with evolution of carbon dioxide and formation of homorcinol.[3]

β-Erythrin or *Homo-erythrin*, $C_{21}H_{24}O_{10}+H_2O$, was discovered in a stunted specimen of *R. fuciformis*.[4] It crystallizes in concentrically arranged needles, which are very readily soluble in alcohol. On boiling with baryta water it is resolved into carbon dioxide, erythrol and homorcinol:

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[1] *Ann. Chem. Pharm.* lxviii. 83 ; clv. 56.

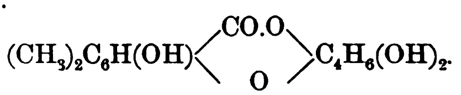
[2] *Ibid.* cxvii. 297.

[3] Stenhouse and Groves, *Journ. Chem. Soc.* 1880, 407.

[4] Menschutkin, *Bull. Soc. Chim.* [2] ii. 424 ; Lamparter, *Ann. Chem. Pharm.* cxxxiv. 234.

$$C_{13}H_{16}O_6 + 2H_2O = CO_2 + C_4H_{10}O_4 + C_8H_{10}O_2.$$

It is not homologous with picroerythrin, but is the anhydride of such a compound, which would probably have the following constitution:



$$(CH_3)_2C_6H(OH)\begin{array}{c}\diagup CO.O \diagdown \\ \diagdown \;\; O \;\; \diagup\end{array}C_4H_6(OH)_2.$$

Picrorocellin, $C_{27}H_{29}N_3O_5$, was found along with erythrin by Stenhouse and Groves in a variety of *R. tinctoria* which probably came from western Africa. It is insoluble in water, tolerably soluble in hot alcohol, and crystallizes in long, lustrous prisms, which melt at 192°—194°, and have an intensely bitter taste. On oxidation with chromic acid, benzoic acid is obtained together with a liquid smelling like benzaldehyde. On dry distillation it yields water, ammonia, and *xanthorocellin*, $C_{21}H_{17}N_2O_2$, which is also obtained by heating picrorocellin with dilute acids, and crystallizes from alcohol in long, yellow needles, melting at 183°.[1]

2234 *Para-orsellinic acid*, $C_6H_2(CH_3)(OH)_2CO_2H + H_2O$, is prepared by heating orcinol with 4 parts of ammonium carbonate and 4 parts of water for 10—15 hours to the boiling-point of amyl alcohol,[2] or by passing carbon dioxide over the potassium compound of orcinol at 250°—260°.[3] It crystallizes from dilute alcohol in fine, hard needles, which dissolve in about 660 parts of cold water; the solution is coloured blue by ferric chloride. On heating the acid it loses water at 100° and commences to melt at about 150° with evolution of carbon dioxide, which is also given off when the acid is simply boiled with water; on dry distillation it decomposes completely with formation of orcinol.

Barium para-orsellinate, $(C_8H_7O_4)_2Ba + 6H_2O$, crystallizes in four-sided tablets, which are readily soluble in water.

Paraphosphorsellinic acid is formed as a chromegreen powder by heating para-orsellinic acid with phosphorus oxychloride (p. 433).

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[1] *Ann. Chem. Pharm.* clxxxv. 14.

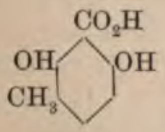
[2] Brunner and Senhofer, *Monatsh.* xiii. 1643.

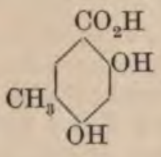
[3] Schwarz, *Ber. Deutsch. Chem. Ges.* xiii. 1643.

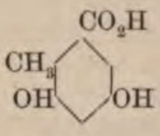
Cresorcinolcarboxylic acid, $C_6H_2(CH_3)(OH)_2CO_2H + H_2O$, is formed when cresorcinol is heated in a small flask with 4 parts of potassium or sodium bicarbonate for half an hour. It is slightly soluble in cold, readily in hot water and alcohol, and crystallizes in very long, thin, lustrous prisms, which lose their water at 100° and melt at 208° with decomposition. Its solution is coloured bluish violet by ferric chloride and is not precipitated by lead acetate.[1]

Cresorsellinic acid, $C_6H_2(CH_3)(OH)_2CO_2H$ (1 : 2 : 4 : 6), is prepared by fusing disulphorthotoluic acid with caustic potash. It is slightly soluble in cold, readily in hot water, and crystallizes in long, hard, vitreous needles, which melt at 245°. It reduces ammoniacal silver solution on heating and Fehling's solution on boiling; its aqueous solution is coloured dark brown by ferric salts, a ferrous compound being formed. On heating with sulphuric acid the liquid assumes a splendid stable magenta colour; water precipitates from it yellow flocks, which form an intense golden-yellow solution in alkalis. It therefore gives a similar reaction to that which is characteristic of the analogous α-resorcylic acid (p. 358). When it is heated to 220°—225° with hydrochloric acid, dark flocks separate out, which form a reddish brown solution in alcohol; on the addition of a little alkali, the liquid takes a splendid dark green fluorescence, which disappears when an excess of alkali is added, a deep purple-red solution being formed. Cresorcinol is formed when the acid is distilled with slaked lime.[2]

Three carboxylic acids are derived from cresorcinol:







The last of these expresses the constitution of cresorsellinic acid, which is a derivative of orthotoluic acid. The second probably represents that of cresorcinolcarboxylic acid, since the readiness with which it is formed supports the conclusion that the carboxyl takes up the same position in the nucleus in the case of cresorcinol as it does in the analogous formation of β-resorcylic acid from resorcinol (p. 359).

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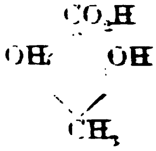
[1] Kostanecki, *Ber. Deutsch. Chem. Ges.* xviii. 3202.

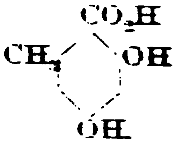
[2] Jacobsen and Wierss, *ibid.* xvi. 1956.

The constitution of para-orsellinic acid, and therefore that of orsellinic acid, follows from these considerations (Kostanecki) :

Orsellinic acid.



Para-orsellinic acid.



2235 *Homohydroxysalicylic acid*, $C_6H_2(CH_3)(OH)_2CO_2H$, is prepared by heating 40 grms. of toluquinol for thirty-six hours in a bath of oil of turpentine with 130 grms. of potassium bicarbonate, 110 ccs. of water, and 40 ccs. of a saturated solution of potassium sulphite. It dissolves in 1,366 parts of water at 8°, more readily in hot water, and crystallizes from dilute alcohol in microscopic, acute rhombic plates, while, when prepared from the ammoniacal salt by precipitation with hydrochloric acid, it separates as a crystalline powder containing half a molecule of water. Ferric chloride produces an azure-blue colouration, which passes into a beautiful green on standing or on the addition of an excess of the chloride; it reduces Fehling's solution on warming, but a neutral silver solution in the cold. It is decomposed at 210°—220° into carbon dioxide and toluquinol.[1]

Barium homohydroxysalicylate, $(C_8H_7O_4)_2Ba + 2H_2O$, forms fine prismatic needles, readily soluble in water.

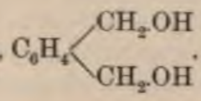
Creosolcarboxylic acid, $C_6H_2(CH_3)(OCH_3)(OH)CO_2H$ (1:3:4:5). According to the researches of Kostanecki, only those phenols which contain hydroxyl groups in the meta-position are converted into carboxylic acids by boiling with the alkali bicarbonates, and as creosol does not belong to this class of bodies, the corresponding acid is prepared by adding sodium, warming gently and passing in a current of carbon dioxide.

Creosolcarboxylic acid crystallizes from a mixture of chloroform and benzene in concentrically arranged needles, which melt at 180°—182° and sublime when carefully heated. It is readily soluble in alcohol, ether and chloroform, but only slightly in water and scarcely at all in benzene and petroleum ether; its solution is coloured deep blue by ferric chloride. The barium salt crystallizes in small, anhydrous needles, which are only slightly soluble in water.

nner, *Monatsh. Chem.* ii. 458.

Methyl creosolcarboxylate, $C_6H_4(CH_3)(OCH_3)(OH)CO_2.CH_3$, forms small, rhombic prisms, melts at 92° and gives a bluish green colouration with ferric chloride.[1]

XYLYLENE ALCOHOLS, C_6H_4



$$C_6H_4\left\langle\begin{matrix}CH_2.OH\\CH_2.OH\end{matrix}\right..$$

2236 *Orthoxylylene alcohol* was first prepared by the action of sodium amalgam on a boiling solution of phthalyl chloride, $C_6H_4.C_2O_2Cl_2$ (p. 458), in glacial acetic acid, and named *phthalalcohol*.[2] It is also obtained by boiling its bromide with a solution of sodium carbonate[3] or potassium carbonate.[4] It is tolerably soluble in water, readily in alcohol, and crystallizes in rhombic tablets, which have a bitter taste and melt at 64·5°. Concentrated sulphuric acid imparts to them a red colour and then converts them into a resinous mass. Potassium permanganate or chromic acid oxidize it to phthalic acid, while it is reduced to orthoxylene by heating with hydriodic acid and amorphous phosphorus.

Orthoxylylene ethyl ether, $C_6H_4(CH_2OC_2H_5)_2$, is obtained by boiling the bromide with alcoholic potash, and is a very pleasant-smelling, oily liquid, which boils at 247°—249° (Leser).

Orthoxylylene chloride, $C_6H_4(CH_2Cl)_2$, is formed when ten ccs. of orthoxylene are heated to 190° with 35 grms. of phosphorus pentachloride,[5] as well as by heating the alcohol with hydrochloric acid, and separates from ether in crystals, which melt at 54·8° and readily sublime. Its vapour attacks the eyes with great violence.

Raymann, by the action of chlorine on boiling orthoxylene, obtained an isomeric substance, which crystallizes in tablets and melts at 103°.[6] These properties correspond with those of paraxylylene chloride, and the hydrocarbon employed by Raymann must have contained paraxylene, which is much more readily attacked by chlorine and bromine than its isomerides. This property can be made use of to detect even traces of paraxylene in the presence of the ortho- and meta- compounds; the mixture is treated at the boiling point with sufficient bromine to form the monobromo-derivatives; any paraxylene present is converted into paraxylylene bromide, which separates out on cooling.[1]

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[1] Wende, *Ber. Deutsch. Chem. Ges.* xix. 2324.

[2] Hessert, *ibid.* xii. 642.

[3] Baeyer and Perkin, xvii. 122.

[4] Colson, *Ann. Chim. Phys.* [6] vi. 104.

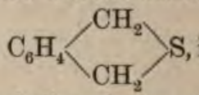
[5] Colson and Gautier, *Bull. Soc. Chim.* xlv. 6; Colson, *Ann. Chim. Phys.* [6] i. 108.

[6] *Bull. Soc. Chim.* xxvi. 553.

Orthoxylylene bromide, $C_6H_4(CH_2Br)_2$ is obtained when orthoxylene is heated with the calculated quantity of bromine to 150°—155°, or when the latter is allowed to drop into the boiling hydrocarbon, the temperature being gradually raised to 180°. It is also formed when orthoxylene is treated with bromine in the sunlight,[2] and crystallizes from chloroform in splendid, rhombic pyramids, which melt at 94·9°, and dissolve in 5 parts of ether.

Orthoxylylene iodide, $C_6H_4(CH_2I)_2$, is prepared by heating the alcohol with phosphorus and hydriodic acid, and crystallizes from ether in splendid, well-formed yellowish prisms, melting at 109°—110°.[3]

Orthoxylylene acetate, $C_6H_4(CH_2O.CO.CH_3)_2$, is formed by the action of acetyl chloride on the alcohol; it is a crystalline mass, which melts at 37° and boils without decomposition.

Orthoxylylene sulphide,  $C_6H_4{<}\begin{matrix}CH_2\\CH_2\end{matrix}{>}S$, is obtained by heating the bromide with an alcoholic solution of potassium sulphide, and is a colourless liquid which smells like mercaptan and solidifies in large crystals at about 0° (Leser).

Diphenylorthoxylylenediamine, $C_6H_4(CH_2.NH.C_6H_5)_2$, is prepared by the action of aniline on the bromide. It crystallizes from alcohol in small plates, melting at 172°, and dissolves in concentrated hydrochloric acid, but is reprecipitated by water.

Metaxylylene alcohol, $C_6H_4(CH_2.OH)_2$. This compound, which is also known as *isophthalalcohol*, is prepared by heating the bromide with a solution of carbonate of potassium. It is readily soluble in water and separates from ether as an oily liquid, which solidifies to microscopic, twinned crystals, melting at 46°—47°.[4]

Metaxylylene ethyl ether is obtained by heating the bromide with alcoholic potash, and is an oily liquid, which boils at 247°—249°, and is oxidized by chromic acid to isophthalic acid.[5]

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[1] Radziszewski and Wispek, *Ber. Deutsch. Chem. Ges.* xviii. 1279.
[2] Schramm, *ibid.* xviii. 1272.
[3] Leser, *ibid.* xvii. 1824.
[4] Colson, *Ann. Chim. Phys.* [6] vi. 109.
[5] W. H. Perkin, jun., Private communication.

Metaxylylene chloride, $C_6H_4(CH_2Cl)_2$, is prepared by heating the alcohol with hydrochloric acid (Colson); it is also formed when metaxylene is heated with phosphorus pentachloride, the yield being, however, very poor (Colson and Gautier). It crystallizes in pointed prisms, melts at 34° and boils at 250°—255°.[1]

Metaxylylene bromide, $C_6H_4(CH_2Br)_2$, forms long, prismatic needles, melting at 77°, and is obtained by heating metaxylene with bromine (Colson, Radziszewski and Wispek), as well as by bringing these two substances together in the sunlight (Schramm).

Paraxylylene alcohol, $C_6H_4(CH_2.OH)_2$, was prepared by Grimaux by heating the chloride or bromide with 30 parts of water to 170°—180°, and was named *tollylene glycol*.[2] It crystallizes in lustrous needles, which melt at 112°—113°, are readily soluble in water, alcohol and ether, and are converted by oxidation into terephthalic acid.

Paraxylylene mono-ethyl ether, $C_6H_4(CH_2.OH)CH_2.O.C_2H_5$, is formed when the chloride is heated with alcoholic potash; it is a pleasant-smelling liquid which boils at 250°—252°.[3]

Paraxylylene chloride, $C_6H_4(CH_2Cl)_2$, is prepared by the action of chlorine on boiling paraxylene,[4] or by heating the alcohol with hydrochloric acid. It may also be obtained in a similar manner to the ortho-compound by heating paraxylene with phosphorus pentachloride (Colson and Gautier). It crystallizes from alcohol in pointed, rhombic tablets, melts at 100° and boils with decomposition at 240°—250°.

Paraxylylene bromide, $C_6H_4(CH_2Br)_2$, is obtained by passing bromine vapour into paraxylene or by heating the alcohol with hydrobromic acid; it boils at 240°—250°, and crystallizes from chloroform in plates, which melt at 143·5°,[5] and dissolve in about 50 parts of ether.

Paraxylylene iodide, $C_6H_4(CH_2I)_2$, is prepared by heating the alcohol with hydriodic acid; it forms fine needles, which melt at 170°, and rapidly become coloured yellow in the air.

Paraxylylene acetate, $C_6H_4(CH_2.O.CO.CH_3)_2$, is formed when the chloride is heated to 150° with an alcoholic solution of sodium acetate. It is readily soluble in alcohol and ether, and crystallizes from the latter in hard, lustrous plates, which have a pungent, camphor-like taste, and melt at 47°.

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[1] *Bull. Soc. Chim.* xliii. 6.

[2] *Ann. Chem. Pharm.* clv. 338.

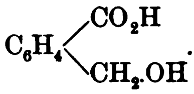
[3] Grimaux, *Bull. Soc. Chim.* xvi. 193.

[4] Grimaux, *Zeitschr. Chem.* 1867, 381.

[5] Radziszewski and Wispek, *Ber. Deutsch. Chem. Ges.* xviii. 1280; Löw, *ibid.* xviii. 2072.

Paraxylylene monobenzoate, $C_6H_4.(CH_2.OCO.C_6H_5)CH_2.OH$, is obtained by heating the chloride with an alcoholic solution of sodium benzoate, and crystallizes in long, thin needles, melting at 73°—74°.

HYDROXYMETHYLBENZOIC ACIDS,



$$C_6H_4\begin{cases}CO_2H\\CH_2.OH\end{cases}.$$

2237 These compounds are isomeric with the hydroxytoluic acids, from which they differ in being alcohols while the latter are phenols.

Parahydroxymethylbenzoic acid was prepared by Dittmar and Kekulé, who named it oxymethylphenylformic acid, by heating paratoluic acid with bromine at 160°—170°, and boiling the product with baryta water. It crystallizes in white plates or flat needles, which are more readily soluble in water than paratoluic acid, melt a few degrees higher and sublime in feathery needles.[1]

Orthohydroxymethylbenzoic acid was first prepared by Hessert, who named it "*Benzolorthoalcoholsäure*," by the action of alkalis on phthalide, which is its anhydride. Acids precipitate it as a fine powder, which is slightly soluble in cold water, readily in alcohol, has a strongly acid reaction, and melts at 118°, being thus converted into the anhydride, which is also formed when the acid is simply boiled with water.

Silver orthohydroxymethylbenzoate, $C_8H_7O_3Ag$, crystallizes from water in small octohedra.

Phthalide, $C_8H_6O_2$, was obtained by Kolbe and Wischin, who prepared it by the action of zinc and hydrochloric acid on phthalyl chloride, $C_8H_4O_2Cl_2$, and named it *phthalaldehyde*, $C_6H_4(COH)_2$.[2] It is also formed by the action of phosphorus and hydriodic acid on the chloride,[3] and when orthoxylidene chloride is boiled with water and lead nitrate.[4] Hessert has proved that it is not the aldehyde of phthalic acid but the anhydride or lactone of the preceding compound.[1] Its formation was explained by the following reactions:

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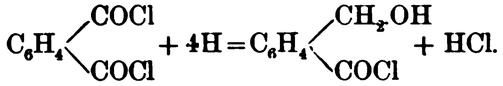
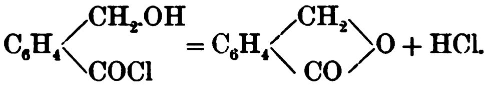
[1] *Ann. Chem. Pharm.* clxii. 337.
[2] *Zeitschr. Chem.* 1866, 315.
[3] Baeyer, *Ber. Deutsch. Chem. Ges.* x. 123.
[4] Raymann, *Bull. Soc. Chim.* x. 1180.

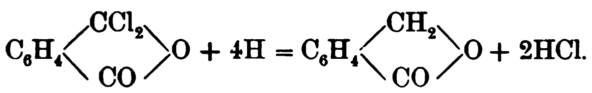


$$C_6H_4\left\langle\begin{matrix}COCl\\COCl\end{matrix}\right. + 4H = C_6H_4\left\langle\begin{matrix}CH_2.OH\\COCl\end{matrix}\right. + HCl.$$



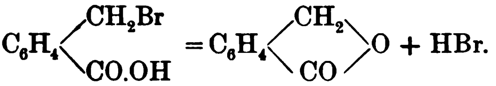
$$C_6H_4\left\langle\begin{matrix}CH_2.OH\\COCl\end{matrix}\right. = C_6H_4\left\langle\begin{matrix}CH_2\\CO\end{matrix}\right\rangle O + HCl.$$

It has since been shown that phthalyl chloride has not the constitution assumed above (p. 460), and the formation of phthalide is now represented much more simply:



$$C_6H_4\left\langle\begin{matrix}CCl_2\\CO\end{matrix}\right\rangle O + 4H = C_6H_4\left\langle\begin{matrix}CH_2\\CO\end{matrix}\right\rangle O + 2HCl.$$

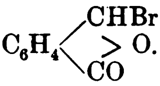
This is confirmed by the observation of Hjelt, who found that it is also obtained when bromine is passed into orthotoluic acid heated to 140°; the brominated acid which is first formed being decomposed as follows:[2]



$$C_6H_4\left\langle\begin{matrix}CH_2Br\\CO.OH\end{matrix}\right. = C_6H_4\left\langle\begin{matrix}CH_2\\CO\end{matrix}\right\rangle O + HBr.$$

It crystallizes from boiling water in needles which smell like cinnamon, melts at 73° and boils at 290° (Gräbe). It does not combine with hydroxylamine,[3] gives no compounds with the acid sulphites of the alkalis and does not reduce ammoniacal silver solution (Hessert). It is oxidized to phthalic acid by alkaline permanganate, while it is reduced to orthotoluic acid on heating with phosphorus and hydriodic acid, and to orthoxylene together with a little toluene by heated zinc dust.

Monobromophthalide is formed by the action of bromine vapour on heated phthalide; it crystallizes in plates, melting at 86°, and is converted into phthalaldehydic acid (p. 447) when heated with water; it has, therefore, the following constitution:[4]



$$C_6H_4\left\langle\begin{matrix}CHBr\\CO\end{matrix}\right\rangle O.$$

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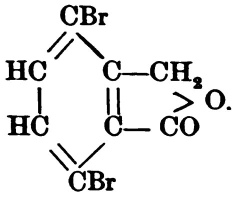
[1] *Ber. Deutsch. Chem. Ges.* x. 1445; xi. 237.

[2] *Ibid.* xix. 412.

[3] Lach, *ibid.* xvi. 1782.

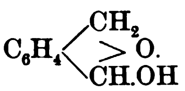
[4] Racine, ibid. xix. 778.

Dibromophthalide, $C_8H_4Br_2O_2$, is obtained, together with dibromonaphthoquinone, by the oxidation of α-dibromonaphthalene with chromic acid, and crystallizes from boiling alcohol in hard, white prisms, which sublime in needles and melt at 187·5°; it does not reduce ammoniacal silver solution and only dissolves slowly in boiling caustic soda solution.[1] It has the following constitution:



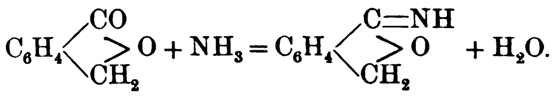
Guareschi obtained dichlorophthalide in a similar manner from dichloronaphthalene; it resembles the bromine compound, and melts at 163°.[2]

Hydrophthalide, $C_8H_8O_2$, is formed together with phthalylpinacone, $C_{16}H_{18}O_4$, by the action of sodium amalgam on an acid solution of phthalide, and is a syrupy mass, extremely soluble in all solvents; it probably has the following constitution (Hessert):



$$C_6H_4\left\langle\begin{matrix}CH_2\\ CH.OH\end{matrix}\right\rangle O.$$

Phthalimidine, C_8H_7NO, is obtained by heating phthalide with zinc ammonium chloride, or by treating it at its boiling-point with ammonia:



$$C_6H_4\left\langle\begin{matrix}CO\\ CH_2\end{matrix}\right\rangle O + NH_3 = C_6H_4\left\langle\begin{matrix}C{=}NH\\ CH_2\end{matrix}\right\rangle O + H_2O.$$

It may be more simply prepared by the action of tin and hydrochloric acid on phthalimide, $C_6H_4(C_2O_2)NH$. It is readily soluble in alcohol and hot water, crystallizes in prisms or needles, melts at 150° and boils at 337°. When sodium nitrite is added to its solution in hydrochloric acid, yellow needles of *nitrosophthalimidine* separate out; they melt at 156°, and are rapidly converted into orthohydroxymethylbenzoic acid by the action of aqueous caustic soda:

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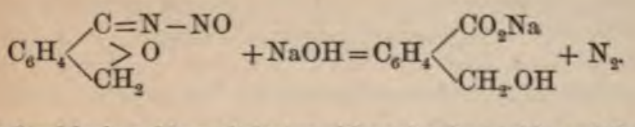
[1] Guareschi, *Ann. Chem. Pharm.* ccxxii. 282.

[2] *Ber. Deutsch. Chem. Ges.* xix. 1155.

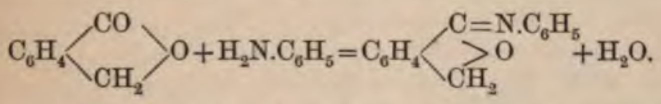


$$C_6H_4\left<\begin{matrix}C{=}N{-}NO\\ >O\\ CH_2\end{matrix}\right. + NaOH = C_6H_4\left<\begin{matrix}CO_2Na\\ \\ CH_2.OH\end{matrix}\right. + N_2.$$

Hydrochloric acid precipitates either the free acid or phthalide from this solution according to the temperature, and the latter substance is in fact most conveniently prepared in this way from phthalimide, which can itself be readily obtained from phthalic acid.[1]

Methylphthalimidine, $C_8H_6O(NCH_3)$, is formed by the action of tin and hydrochloric acid on methylphthalimide, and is readily soluble in water, alcohol and ether, from which it crystallizes in large tablets, melting at 120°; it boils without decomposition at about 300°.[2]

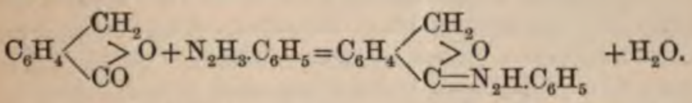
Phenylphthalimidine or *Phthalide-anil* is prepared by heating phthalide to 200°—220° with aniline:



$$C_6H_4\left<\begin{matrix}CO\\ \\ CH_2\end{matrix}\right>O + H_2N.C_6H_5 = C_6H_4\left<\begin{matrix}C{=}N.C_6H_5\\ >O\\ CH_2\end{matrix}\right. + H_2O.$$

It crystallizes from alcohol in silvery plates, melting at 160° (Hessert).

Phthalidehydrazide, $C_{14}H_{12}N_2O$, is formed by heating phthalide with phenylhydrazine for some time:



$$C_6H_4\left<\begin{matrix}CH_2\\ >O\\ CO\end{matrix}\right. + N_2H_3.C_6H_5 = C_6H_4\left<\begin{matrix}CH_2\\ >O\\ C{=}N_2H.C_6H_5\end{matrix}\right. + H_2O.$$

It crystallizes from hot water or alcohol in needles, which possess a silver lustre, and melt at 165°.[3]

Paranitrophthalide, $C_8H_5(NO_2)O_2$, is prepared by dissolving 20 grms. of phthalide in 200 grms. of sulphuric acid, and running in a solution of rather more than the calculated quantity of potassium nitrate in 80 grms. of sulphuric acid, the solution being well cooled during the operation. It forms long, colourless needles, which melt at 141°, and are almost insoluble in cold water, but dissolve slightly on boiling, more readily in alcohol, and readily in benzene. Alcoholic potash produces a characteristic violet colouration, while aqueous potash forms a yellow solution. Dilute sulphuric acid precipitates *paranitrohydroxymethylbenzoic acid*, $C_6H_3(NO_2)(CH_2.OH)CO_2H$, from the cool solution. This body crystallizes in microscopic needles united in stellate forms, and is extremely soluble in ether, readily in alcohol and hot water. It melts at 129°, and decomposes at a higher temperature into water and nitrophthalide.

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[1] Gräbe, *Ber. Deutsch. Chem. Ges.* xvii. 2598; xviii. 1408.

[2] Gräbe and Pictet, *ibid.* xviii. 1173.

[3] V. Meyer and Münchmeyer, *ibid.* xix. 1706 and 2132.

Paramidophthalide, $C_8H_5(NH_2)O_2$, is obtained by the reduction of the preceding compound, and is almost insoluble in water, but dissolves slightly in alcohol, and more readily in chloroform, from which it crystallizes in short prisms, melting at 178°. Its hydrochloride forms needles which are readily soluble in water. It also dissolves in alkalis, salts of *paraamidohydroxymethylbenzoic acid* being formed. The free acid has not yet been prepared.

When paranitrophthalide is heated with hydriodic acid and phosphorus, γ-amido-orthotoluic acid is formed.[1]

Orthonitrophthalide was prepared by Beilstein and Kurbatow, together with the corresponding nitrophthalic acid, by oxidizing α-nitronaphthalene with a solution of chromium trioxide in acetic acid. They mention that the substance obtained has the formula of nitrophthalaldehyde, but must possess a different constitution, because it is only attacked with difficulty by the oxidizing mixture just named.[2] Its properties prove that it is actually orthonitrophthalide.[3]

It crystallizes in small plates, melting at 136°, is much more readily soluble in alcohol and chloroform than the para-compound, and forms a yellow solution in alkalis. On heating in a sealed tube with dilute hydrochloric acid, it is smoothly converted into v-nitrophthalic acid (Hönig).

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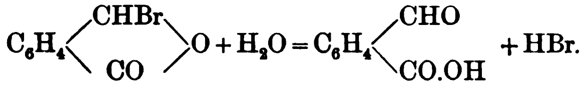
[1] Hönig, *Ber. Deutsch. Chem. Ges.* xviii. 3447.
[2] *Ann. Chem. Pharm.* ccii. 217.
[3] Guareschi, *ibid.* ccxxii. 283; Hönig, *loc. cit.*

ALDEHYDES, $C_6H_4(CHO)_2$, AND ALDEHYDO-ACIDS, $C_6H_4(COH)(COOH)$.

2238 *Phthalaldehyde.* When orthoxylene is submitted at the boiling-point to the continued action of chlorine, or is heated to 195° with eight parts of phosphorus pentachloride, *orthoxylidene tetrachloride*, $C_6H_4(CHCl_2)_2$, is formed; it crystallizes from ether in large asymmetric prisms, melts at 89° and boils at 273°—274°. On heating with water it is converted into phthalaldehyde, which is also formed by the oxidation of phthal alcohol, and is an oily liquid, which has not yet been prepared pure since it so readily passes into the isomeric phthalide (Hjelt). According to Colson and Gautier, phthalaldehyde is a yellow crystalline substance melting at 52°. Ammonia produces a deep blue or yellow colouration, followed by a brown precipitate.[1]

Phthalaldehydic acid is prepared by heating monobromophthalide with water:[2]



$$C_6H_4{<}\begin{matrix}CHBr\\CO\end{matrix}{>}O + H_2O = C_6H_4{<}\begin{matrix}CHO\\CO.OH\end{matrix} + HBr.$$

It may also be obtained by heating orthoxylene to 200 with 12·5 parts of phosphorus pentachloride and boiling the product, *xylidenyl pentachloride*, $C_6H_4(CHCl_2)CCl_3$, with water (Colson and Gautier). It forms lemon-yellow crystals, which melt at 98° to 100°, and are readily soluble in water. Its phenylhydrazine compound crystallizes in fine, yellow needles.

Isophthalaldehyde is prepared in a similar manner from *metaxylidene tetrachloride*, $C_6H_4(CHCl_2)_2$, which is a liquid boiling at 273°. It is an oily liquid which, as well as its solution in water, gives a green colouration with ammonia, followed by a brown precipitate (Colson and Gautier).

Terephthalaldehyde, $C_6H_4(CHO)_2$, was obtained by Grimaux from paraxylylene chloride, $C_6H_4(CH_2Cl)_2$, by boiling with lead nitrate and water,[3] while Löw prepared it by the same method from paraxylylene bromide.[4]

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[1] Hjelt, *Ber. Deutsch. Chem. Ges.* xviii. 2879; xix. 411; Colson and Gautier, *Bull. Soc. Chim.* xlv. 6 and 506.

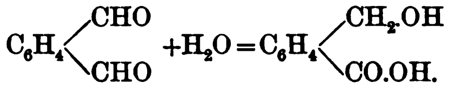
[2] Racine, *Ber. Deutsch. Chem. Ges.* xix. 778.

[3] *Jahrsber. Chem.* 1876, 490; Colson and Gautier, *loc. cit.*

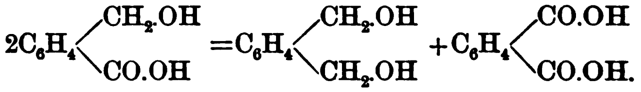
[4] *Ann. Chem. Pharm.* ccxxxi. 361.

It is also formed when paraxylene is heated to 190° with eight parts of phosphorus pentachloride, and the *paraxylidene tetrachloride* which is thus formed boiled with water for some time. The latter forms well-developed crystals, melting at 93°.

Terephthalaldehyde is only very slightly soluble in cold ether, but readily in alcohol and tolerably freely in hot water, from which it crystallizes in fine needles, melting at 116°. It forms a readily soluble compound with acid sodium sulphite. Concentrated caustic soda solution decomposes it with formation of parahydroxymethylbenzoic acid, paraxylylene alcohol and terephthalic acid:

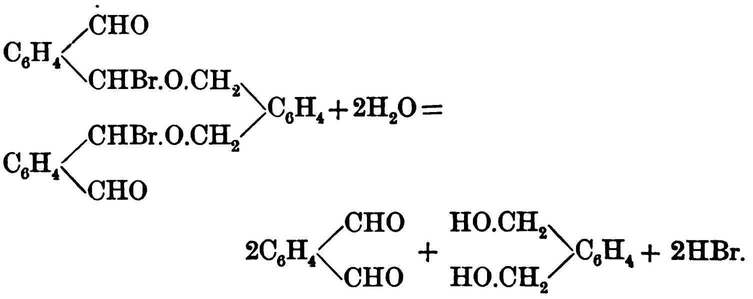


$$C_6H_4\left\langle\begin{matrix}CHO\\CHO\end{matrix}\right. + H_2O = C_6H_4\left\langle\begin{matrix}CH_2.OH\\CO.OH.\end{matrix}\right.$$



$$2C_6H_4\left\langle\begin{matrix}CH_2.OH\\CO.OH\end{matrix}\right. = C_6H_4\left\langle\begin{matrix}CH_2.OH\\CH_2.OH\end{matrix}\right. + C_6H_4\left\langle\begin{matrix}CO.OH\\CO.OH.\end{matrix}\right.$$

Terephthalaldehyde is also obtained when paraxylylene bromide is dissolved in cold, concentrated nitric acid. The compound $C_{24}H_{20}Br_2O_4$ is simultaneously formed; it is insoluble in water, but dissolves readily in ether, from which it crystallizes in stunted needles, which melt at 80° and are converted into terephthalaldehyde, paraxylylene alcohol and hydrobromic acid, by heating with water:



$$\begin{matrix}C_6H_4\left\langle\begin{matrix}CHO\\CHBr.O.CH_2\end{matrix}\right.\\C_6H_4\left\langle\begin{matrix}CHBr.O.CH_2\\CHO\end{matrix}\right.\end{matrix}\!\!\!\!\left.\begin{matrix}\\ \\ \end{matrix}\right\rangle C_6H_4 + 2H_2O =$$

$$2C_6H_4\left\langle\begin{matrix}CHO\\CHO\end{matrix}\right. + \left.\begin{matrix}HO.CH_2\\HO.CH_2\end{matrix}\right\rangle C_6H_4 + 2HBr.$$

It is noteworthy that concentrated nitric acid exerts an oxidizing action upon paraxylylene bromide, and does not effect nitration as in the case of benzyl chloride.[1]

Xylylidenediamine, $C_8H_8N_2$, is deposited in very brittle, vitreous crystals when an alcoholic solution of terephthalaldehyde is saturated with ammonia and allowed to stand:

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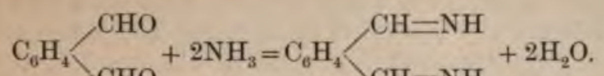
[1] Löw, *Ber. Deutsch. Chem. Ges.* xviii. 2072.



$$C_6H_4\begin{cases}CHO\\CHO\end{cases} + 2NH_3 = C_6H_4\begin{cases}CH{=}NH\\CH{=}NH\end{cases} + 2H_2O.$$

It is also formed when dry ammonia is passed over the aldehyde, but is decomposed again by acids, or even on boiling with water, into ammonia and the aldehyde.

Hydrobenzamide trialdehyde, $N_2(CH.C_6H_4.CHO)_3$, is formed by the action of aqueous ammonia on terephthalaldehyde, as a white powder consisting of matted microscopic needles, which is insoluble in water and alcohol and is dissolved by acids, the aldehyde being set free.[1]

Nitroterephthalaldehyde, $C_6H_3(NO_2)(CHO)_2$. In order to prepare this substance, a solution of the aldehyde heated to 150° is treated with an equal quantity of potassium nitrate dissolved in sulphuric acid, kept at a temperature of 110°—115° for 10—15 minutes, poured into water and then extracted with ether. It is very readily soluble in alcohol, with greater difficulty in hot water and ether, crystallizing from the latter in rhombohedra, which melt at 86° and sublime in large needles. A blue indigo derivative is formed when it is heated with caustic soda and acetone (p. 146) (Löw).

Terephthalaldehydic acid, $C_6H_4(CHO)CO_2H$, is formed, together with terephthalic acid, by the oxidation of the aldehyde with chromic acid solution. It is only slightly soluble in ether and chloroform, and still less readily in hot water, from which it crystallizes in needles, which melt at 246° and sublime in well-formed needles. It forms a barium salt which is readily soluble in water, as well as a scarcely soluble silver salt, and only reduces ammoniacal silver solution after continued boiling.

The ethyl ether, $C_6H_4(CHO)CO_2.C_2H_5$, forms groups of pointed needles, easily reduces ammoniacal silver solution on heating, and gives all the reactions of benzaldehyde (Löw).

Hydrobenzamidetricarboxylic acid, $N_2(CH.C_6H_4.CO_2H)_3$ is not formed by the action of ammonia on the aldehydo-acid, but by the oxidation of the trialdehyde with potassium permanganate. It crystallizes in nacreous, rhombohedral tablets (Oppenheimer).

Nitroterephthalaldehydic acid, $C_6H_3(NO_2)(CHO)CO_2H(2:1:4,$

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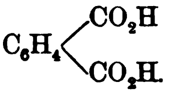
[1] Oppenheimer, *Ber. Deutsch. Chem. Ges.* xix. 574.

is prepared in a similar manner to nitrophthalaldehyde. It is readily soluble in hot water, and crystallizes from it in large, four-sided needles, which melt at 160°. On heating with caustic soda solution and acetone it is converted into indigocarboxylic acid, $C_{16}H_8N_2O_2(CO_2H)_2$, a reaction which proves that the nitroxylyl-group stands in the ortho-position with respect to the aldehyde group.

In its preparation a small quantity of the isomeric acid ($NO_2 : COH : CO_2H = 3 : 1 : 4$), which melts at 184°, is also formed (Löw).

THE PHTHALIC ACIDS,



$C_6H_4<^{CO_2H}_{CO_2H}.$

2239 In the year 1836, Laurent prepared ***naphthalic acid*** (*acide naphtalique*), $C_{10}H_6O_5$, by boiling naphthalene tetrachloride, $C_{10}H_8Cl_4$, with nitric acid,[1] and Marignac, who was subsequently confirmed by Laurent, proposed for it the formula $C_8H_6O_4$. The latter chemist found that it is also obtained, together with other products, by boiling naphthalene with nitric acid, oxalic acid being always simultaneously formed.[2] Since it no longer belongs to the naphthalene series, he named it *phthalic acid* (*acide phtalique*).[3] It decomposes on distillation with lime, as was shown by Marignac, into carbon dioxide and benzene.[4]

During his investigation of the colouring matter of madder root, Schunck found that alizarin is converted by oxidation into *alizaric acid*, $C_{14}H_{10}O_7$,[5] which, according to Gerhardt,[6] confirmed by Strecker and Wolff,[7] is identical with phthalic acid. The *naphthesic acid* (*acide naphtesique*), $C_{10}H_6O_4$, which Laurent had obtained by the action of potassium dichromate and sulphuric acid on naphthalene,[8] was also recognized as phthalic acid by Scheibler[9] and F. Lossen, the latter of whom found that it is also formed by the action of potassium permanganate on naphthalene.[10] An isomeric substance was prepared by Cailletet

[1] *Ann. Chim. Phys.* lxi. 114; *Ann. Chem. Pharm.* xix. 38.

[2] *Ibid.* xxxviii. 13.

[3] *Ibid.* xli. 107.

[4] *Ibid.* xlii. 215.

[5] *Ibid.* lxvi. 197.

[6] *Compt. Rend. Trav. Chim.* 1849, 222.

[7] *Ann. Chem. Pharm.* lxxv. 12.

[8] *Revue Scient.* xiv. 560; *Compt. Rend.* xxi. 36.

[9] *Ber. Deutsch. Chem. Ges.* i. 125.

[10] *Zeitschr. Chem.* x. 419; *Ann. Chem. Pharm.* cxliv. 71

in 1847, by heating oil of turpentine (*essence de térébenthine*) with dilute nitric acid, and named on this account terephthalic acid (*acide téréphtalique*).[1] Five years previously, Persoz had obtained cumino-cyminic acid (*acide cumino-cyminique*) by the oxidation of the ethereal oil contained in the seeds of Roman cumin (*Cuminum Cyminum*), but had not analysed it.[2] Hofmann, in attempting to purify cumic acid, $C_{10}H_{12}O_2$, by treatment with dilute sulphuric acid and potassium dichromate, found that it is thus oxidized to *insolinic acid*, $C_9H_8O_4$, which he also obtained from Roman cumin oil, and which, as he pointed out, is very similar to terephthalic acid,[3] these being afterwards shown by H. Müller and Warren de la Rue to be identical.[4]

Fittig then prepared a third acid by the oxidation of isoxylene and named it isophthalic acid.[5]

The methods employed in the determination of the position of the carboxyl groups in these three acids have already been described in detail (Part III., p. 38). Quite recently, however, Nölting has added a very simple proof of their constitution. The three acids can be quantitatively obtained by the oxidation of the three dimethylbenzenes with an alkaline solution of potassium permanganate. Paraxylene yields terephthalic acid and on nitration gives only one mononitroxylene, while orthoxylene is oxidized to phthalic acid and yields two nitro-derivatives. Finally, three nitroxylenes can be obtained from isoxylene, which corresponds to isophthalic acid. The position of the carboxyls is, therefore, in :

Phthalic acid	1:2
Isophthalic acid	1:3
Terephthalic acid	1:4

This proof is exactly analogous to that employed by Körner to determine the positions of the bromine atoms in the three dibromobenzenes, and by Griess in ascertaining the constitution of the diamidobenzenes (Part III., pp. 47, 48).[6]

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[1] *Ann. Chim. Phys.* [3] xxi. 28.

[2] *Journ. Prakt. Chem.* xxiv. 55 ; *Compt. Rend.* xxxiii. 433.

[3] *Ann. Chem. Pharm.* xcvii. 197.

[4] *Ibid.* cxxi. 86.

[5] *Ibid.* cxlviii. 11.

[6] *Ber. Deutsch. Chem. Ges.* xviii. 2687.

PHTHALIC ACID.

2240 This acid is most simply formed by the oxidation of orthoxylene or orthotoluic acid[1] with potassium permanganate or dilute nitric acid.[2] Carius found that it is also obtained in small quantity when benzene or benzoic acid is treated with manganese dioxide and concentrated sulphuric acid in the cold,[3] diphenylbenzene, $C_6H_4(C_6H_5)_2$, being probably the intermediate product (Part III., p. 76). According to Guyard, it is also formed when a mixture of salicylic, formic and sulphuric acids is heated.[4]

Phthalic acid is manufactured from naphthalene, $C_{10}H_8$, which is first converted into the tetrachloride, $C_{10}H_8Cl_4$, by passing chlorine through the fused hydrocarbon, the plant shown in section and elevation in Figs. 2 and 3 being employed. The mass becomes heated to such an extent that the iron vessel containing it has to be cooled by water, the temperature being kept below 160°—170°, above which carbonization takes place. The tetrachloride is also manufactured by grinding naphthalene with water and potassium chlorate, making up the paste into balls, and bringing these, after drying, into concentrated hydrochloric acid. The chlorate may be replaced by bleaching powder which is mixed with naphthalene and pressed into cakes.

One part of the chloride is then heated with 5—6 parts of nitric acid of sp. gr. 1·35 in flat stoneware retorts placed in an air-bath (Figs. 4 and 5).

The vapours which are evolved are condensed and employed in a subsequent operation. The acid may be finally purified by crystallization, but the product is usually distilled and thus immediately converted into the anhydride. The yield amounts to 30 per cent. on the naphthalene.[5]

Phthalic acid is also formed when naphthalene is heated to 130° with 20 parts of nitric acid of sp. gr. 1·15, 40 per cent of the theoretical yield being obtained.[6]

[1] Weith, *Ber. Deutsch. Chem. Ges.* vii. 1057.
[2] Piccard, *ibid.* xii. 579.
[3] *Ann. Chem. Pharm.* cxlviii. 60.
[4] *Bull. Soc. Chim.* xxix. 248.
[5] Schultz, *Steinkohlentheer*, S. 540; s. E. Fischer, *Ber. Deutsch. Chem. Ges.* xi. 735; Depouilly, *Ann.* Chem. Pharm. cxxxvii. 373.
[6] Beilstein and Kurbatow, *Ann.* Chem. Pharm. ccii. 215.

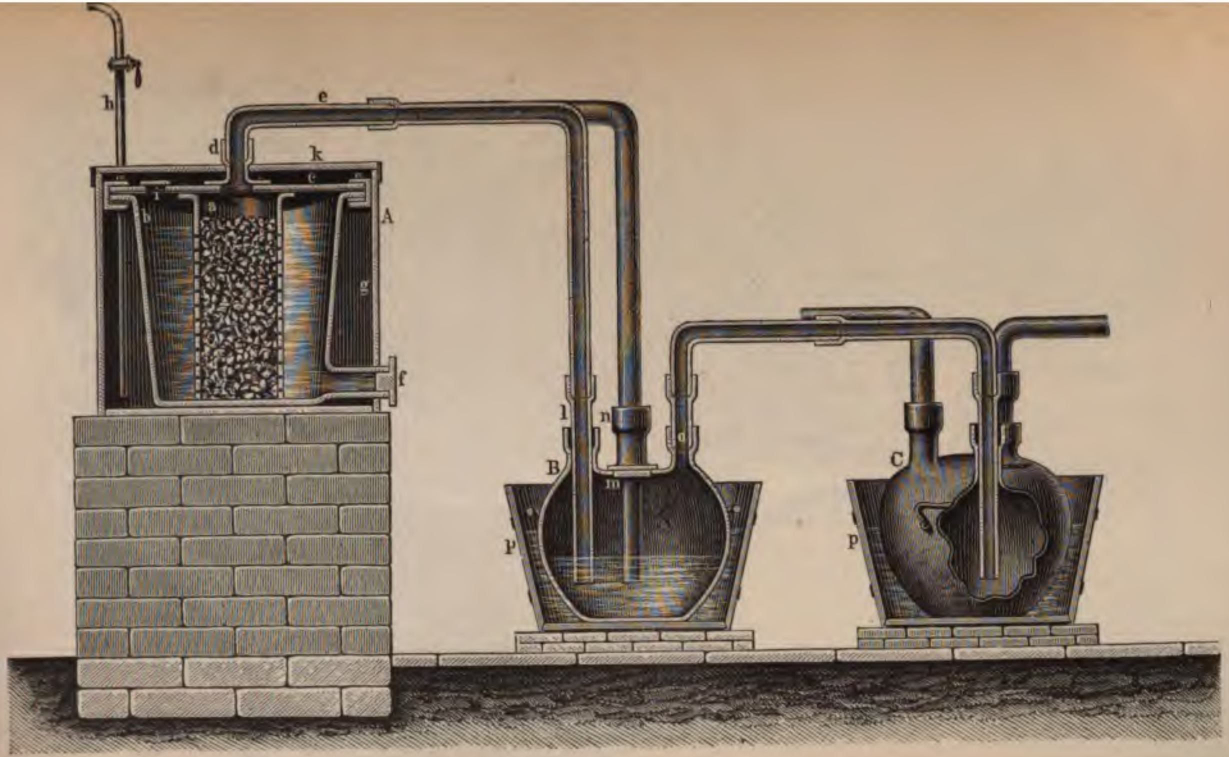

FIG. 2.

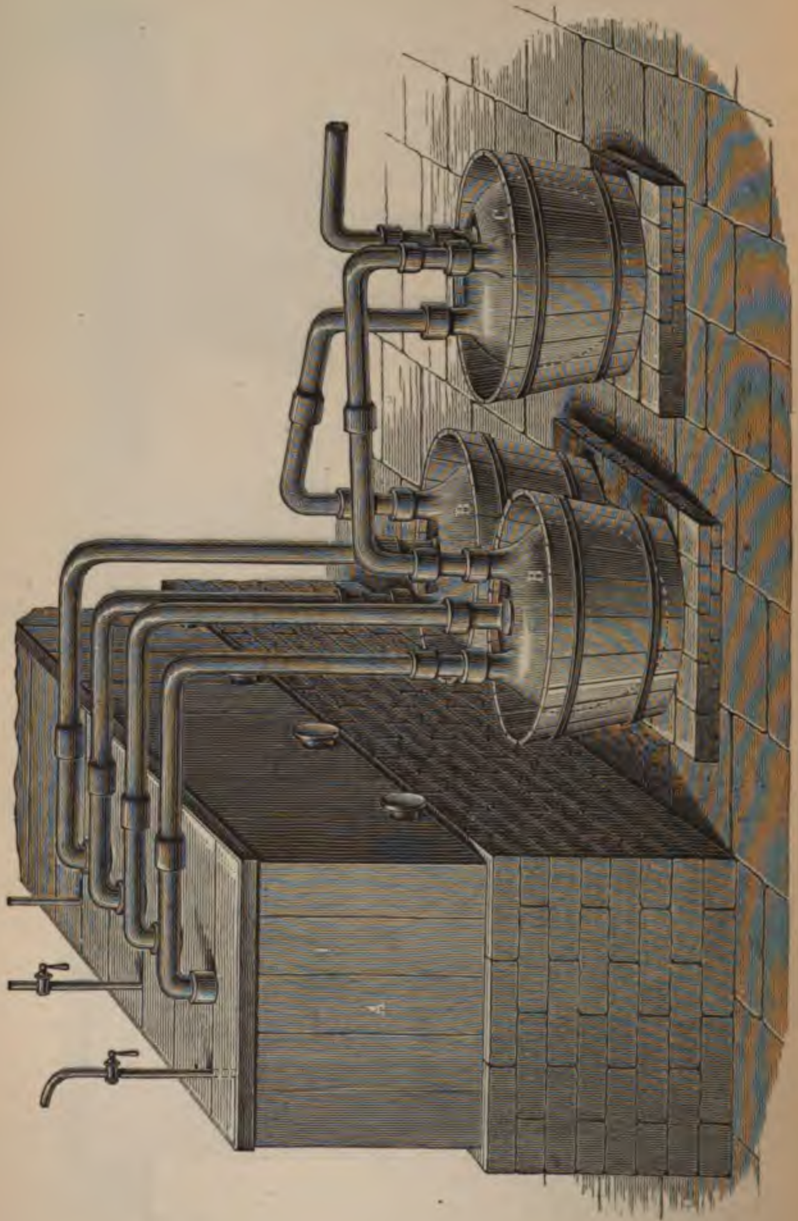

FIG. 3.

Properties. It crystallizes from hot water in thin plates or lustrous, rhombic prisms,[1] which dissolve in 130 parts of water at 11·5°.

100 parts of	ether	absolute alcohol	90 per cent. alcohol,
dissolve at 15°	0·684	10·08	11·70 parts.[2]

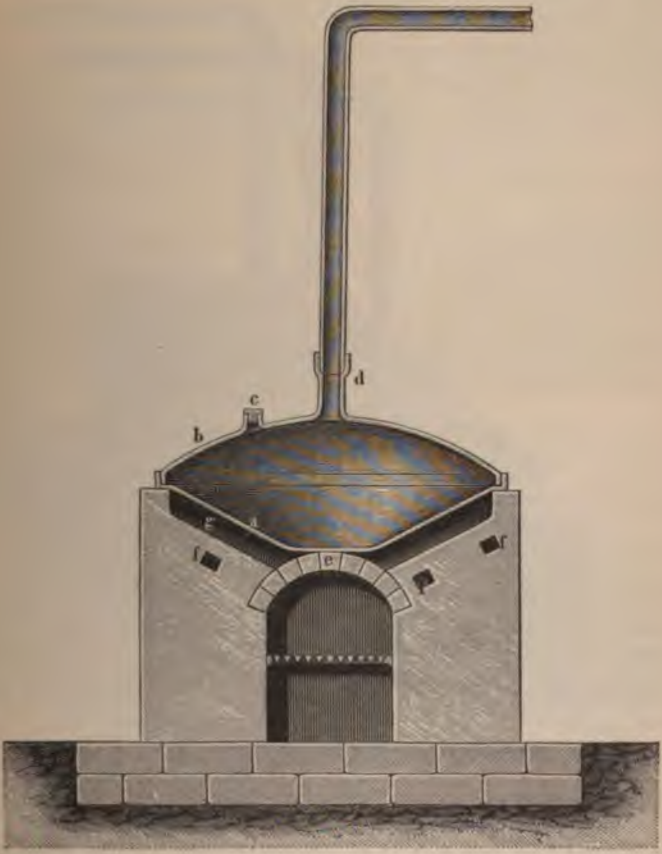

FIG. 4.

Varying statements have been made as to the melting-point of the acid, the discrepancies being due to the fact that it loses water on heating, the anhydride being formed. According to

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[1] Scheibler, *Ber. Deutsch. Chem. Ges.* i. 125; Groth, *Jahresber. Chem.* 1870, 5.
[2] Bourgoin, *Bull. Soc. Chim.* xxix. 247.

Lossen, this takes place at 184°, while Ador states that the unbroken crystals melt at 213°, but the powder at 203°.[1]

It is completely burned by chromic acid solution on heating,[2] and on this account cannot be prepared by means of this reagent from orthoxylene or other ortho-compounds which possess two side chains. On distillation with lime it decomposes into carbon dioxide and benzene, but if the temperature be not allowed to rise above 330°—350°, it is converted into benzoic acid, which was formerly manufactured in this way (p. 155).

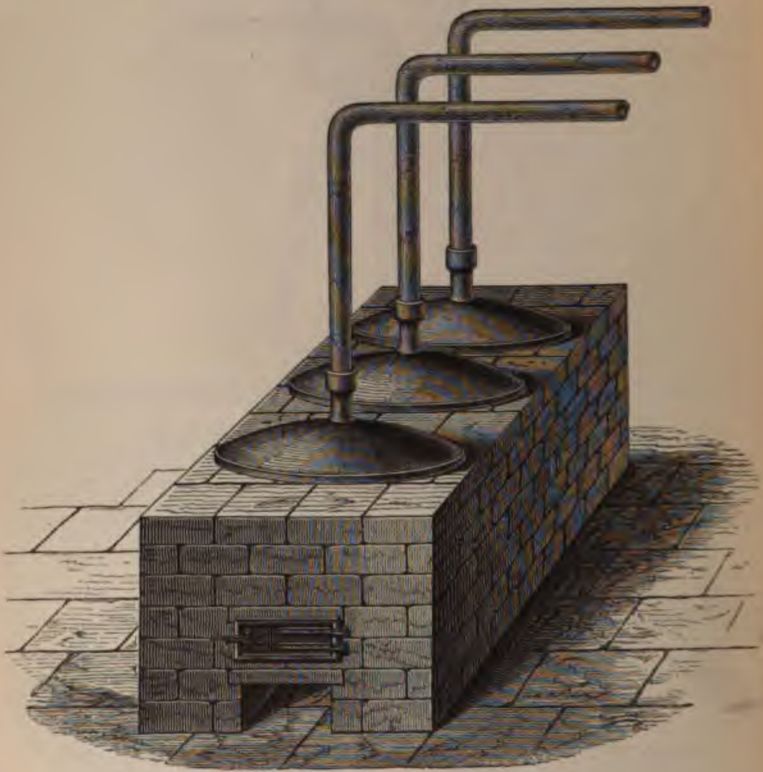

FIG. 5.

2241 The normal phthalates of the alkali metals are readily soluble in water and crystallize in small plates or scales.

Acid ammonium phthalate, $C_8H_5O_4(NH_4)$, separates on the spontaneous evaporation of a solution of the normal salt in six-sided, rhombic tablets, prisms or pyramids, which dissolve very readily in water but only slightly in alcohol.

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[1] *Ann. Chem. Pharm.* clxiii. 230.

[2] Fittig and Bieber, *ibid.* clvi. 242

Calcium phthalate $C_8H_4O_4Ca+H_2O$, is tolerably soluble in water and crystallizes in lustrous, rhombic prisms.[1]

Acid barium phthalate, $(C_8H_5O_4)_2Ba$, is readily soluble in hot water and crystallizes in small, rhombic prisms.

Normal barium phthalate, $C_8H_4O_4Ba$, is obtained by precipitating the normal ammonium salt with barium chloride, or by mixing hot solutions of the acid and caustic baryta; it forms small, white scales or silky needles, which are only slightly soluble in hot water. On evaporating the solution, a basic salt separates out in crystalline crusts (Carius, Hermann).

Lead phthalate, $C_8H_4O_4Pb$, is a precipitate, consisting of scaly crystals.

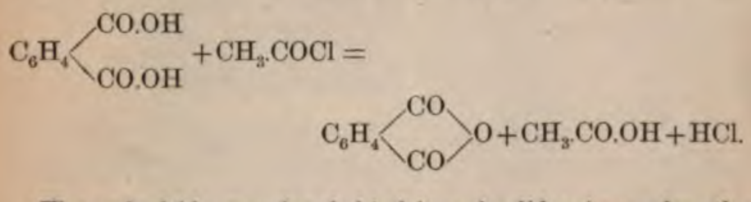
Copper phthalate, $C_8H_4O_4Cu+H_2O$, crystallizes in lustrous blue, rhombic prisms, which dissolve readily in hot water (Hermann).

Silver phthalate, $C_8H_4O_4Ag_2$, forms a light, crystalline powder, which is tolerably soluble in water and detonates when rapidly heated.

Ethers of phthalic acid are formed by the action of hydrochloric acid on the alcoholic solution of the acid and by that of an alcoholic iodide upon the silver salt. The two following have been prepared, and are both odourless liquids:[2]

	Boiling-point.
Methyl phthalate, $C_6H_4(CO_2.CH_3)_2$	280°
Ethyl phthalate, $C_6H_4(CO_2.C_2H_5)_2$	294°

Phthalyl oxide or *Phthalic anhydride*, $(C_6H_4.CO_2)_2O$, is formed when the acid is heated alone or with acetyl chloride:



$$C_6H_4\left\langle\begin{array}{l}CO.OH\\CO.OH\end{array}\right. + CH_3.COCl = C_6H_4\left\langle\begin{array}{l}CO\\CO\end{array}\right\rangle O + CH_3.CO.OH + HCl.$$

The anhydride remains behind in splendid prisms after the acetic acid and excess of acetyl chloride have been removed.[3] It is manufactured by subliming phthalic acid in a current of air, or better, of carbon dioxide, the apparatus shown in Fig. 6 being employed.[1]

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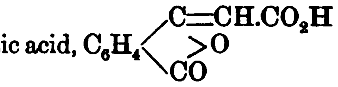
[1] Hermann, *Ann. Chem. Pharm.* cli. 77.

[2] Gräbe and Born, *ibid.* cxlii. 344; Gräbe, *Ber. Deutsch. Chem. Ges.* xvi. 860.

[3] Anschütz, *ibid.* x. 235; *Ann. Chem. Pharm.* ccxxvi. 1.

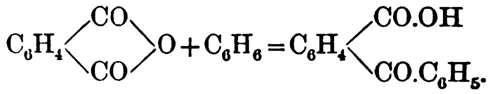
It is thus obtained in long, white, pliant, rhombic needles, while on rapid heating it distils as a liquid and then solidifies to a hard, crystalline mass. It melts at 128° and boils at 284·5° (Schultz, Gräbe), is only very slightly soluble in cold, more readily in hot water, and is reconverted into phthalic acid when boiled with water for a long time, more rapidly in presence of alkalis.

It is reduced by zinc dust and acetic acid to phthalide, diphthalyl (*v. post*) and zinc phthalate being also formed.[2] It is employed in the manufacture of dyes and of many other compounds, as it very readily enters into chemical reactions. Thus it combines with the acid anhydrides, forming with acetic anhydride, phthalylacetic acid,



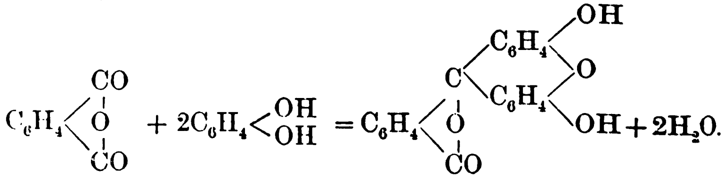
$$C_6H_4\left\langle\begin{matrix} C{=}CH.CO_2H \\ >O \\ CO \end{matrix}\right.$$

It also combines with the aromatic hydrocarbons in presence of aluminium chloride, forming acids; thus benzene yields benzoylbenzoic acid:



$$C_6H_4\left\langle\begin{matrix} CO \\ CO \end{matrix}\right\rangle O + C_6H_6 = C_6H_4\left\langle\begin{matrix} CO.OH \\ CO.C_6H_5. \end{matrix}\right.$$

A specially characteristic property is that of combining with phenols on heating to form *phthaleïns*, water being eliminated. As already mentioned, resorcinol yields fluoresceïn in this way, the formation of this substance, which is employed as a test for the presence of the phenol in question, taking place in the following manner:



$$C_6H_4\left\langle\begin{matrix} CO \\ | \\ O \\ | \\ CO \end{matrix}\right. + 2C_6H_4{<}\begin{matrix} OH \\ OH \end{matrix} = C_6H_4\left\langle\begin{matrix} C\left\langle\begin{matrix} C_6H_4{<}OH \\ >O \\ C_6H_4{<}OH \end{matrix}\right. \\ | \\ O \\ | \\ CO \end{matrix}\right. + 2H_2O.$$

2242 *Phthalyl chloride*, $C_8H_4O_2Cl_2$, was first prepared by Hugo Müller from phthalic acid by the action of phosphorus penta-

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[1] Schultz, *Steinkohlentheer*.

[2] Wislicenus, *Ber. Deutsch. Chem. Ges.* xvii. 2178.

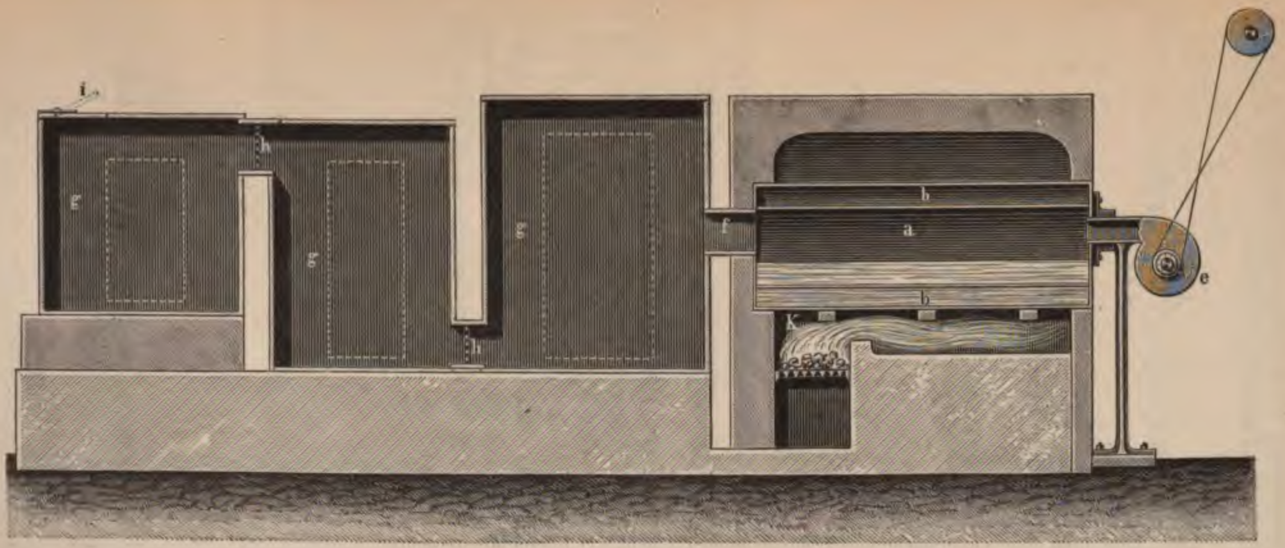
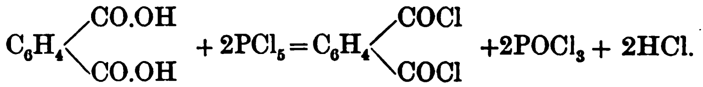


Fig. 6.—Apparatus for the Sublimation of Phthalic Anhydride.

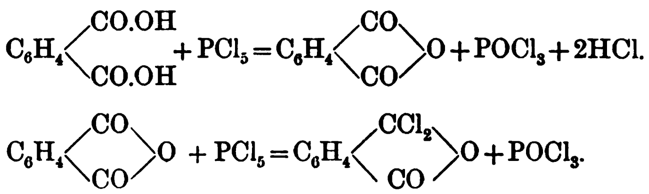
a. Cast iron cylinder to receive the crude phthalic acid: it is surrounded by a wrought iron cylinder *b*, which is partially filled with oil, phenanthrene, &c.—*K.* Fire.—*e.* Ventilating fan to drive the vapours into the wooden chests *g*, which are covered with sacking.—*h.* Coarse wire grating.—*i.* Light, movable trap, covering the exit of the current of air.—The working doors are shown in the figure by dotted lines.

chloride.[1] From analogy with other acid chlorides it would be formed according to the following equation:



$$C_6H_4\left\langle\begin{matrix}CO.OH\\CO.OH\end{matrix}\right. + 2PCl_5 = C_6H_4\left\langle\begin{matrix}COCl\\COCl\end{matrix}\right. + 2POCl_3 + 2HCl.$$

Careful investigation, however, has shown that it does not possess this constitution. It is formed in two stages:

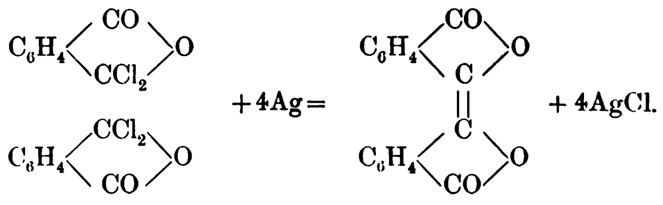


$$C_6H_4\left\langle\begin{matrix}CO.OH\\CO.OH\end{matrix}\right. + PCl_5 = C_6H_4\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle O + POCl_3 + 2HCl.$$

$$C_6H_4\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle O + PCl_5 = C_6H_4\left\langle\begin{matrix}CCl_2\\CO\end{matrix}\right\rangle O + POCl_3.$$

It is also obtained, therefore, when equal molecules of phthalic anhydride and phosphorus pentachloride are heated together for 12 hours at 170°.[2]

In order to prepare it, phthalic acid is boiled with rather more than two molecules of phosphorus chloride for 5–6 hours and then distilled.[3] It is an oily liquid, which boils at 268° and solidifies at about 0°. It is only slowly decomposed by boiling water and even boiling caustic soda solution. On heating with finely-divided silver, *diphthalyl*, which will be subsequently described, is obtained, its formation taking place according to the following equation:



$$\begin{matrix}C_6H_4\left\langle\begin{matrix}CO\\CCl_2\end{matrix}\right\rangle O\\[1em]C_6H_4\left\langle\begin{matrix}CCl_2\\CO\end{matrix}\right\rangle O\end{matrix} + 4Ag = \begin{matrix}C_6H_4\left\langle\begin{matrix}CO\\C\end{matrix}\right\rangle O\\\|\\C_6H_4\left\langle\begin{matrix}C\\CO\end{matrix}\right\rangle O\end{matrix} + 4AgCl.$$

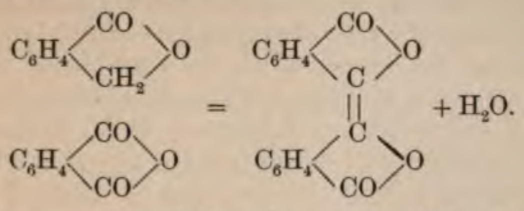
The proof that it possesses this constitution rests not only on the whole behaviour of the substance, which shows it to be a dilac-

[1] *Zeitschr. Chem.* 1863, 257.

[2] Claus and Hoch, *Ber. Deutsch. Chem. Ges.* xix. 1187.

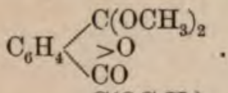
[3] Wischin, *Ann. Chem. Pharm.* cxliii. 259.

tone, but also on the fact that it is formed when phthalide is heated with phthalic anhydride:[1]

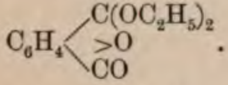


The following compounds have been prepared by the action of sodium methylate and ethylate on phthalyl chloride:

Boiling-point.



. . . . 280°

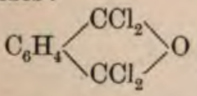


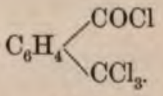
. . . . 294°

These are liquids which boil at the same temperature as the isomeric phthalic ethers, from which they differ only in possessing a slightly lower specific gravity. That they are actually distinct bodies is shown by the fact that tetrachlorophthalic acid yields compounds which differ both in crystalline form and melting point from those derived from its chloride.[2]

The corresponding phenyl ether, $C_6H_4(CO)C(OC_6H_5)_2O$, is prepared by heating the chloride with phenol, and crystallizes from alcohol in small prisms, melting at 70°.[3]

When phthalyl chloride is heated in a sealed tube with phosphorus pentachloride to 210°—220°, two isomeric chlorides, $C_8H_4Cl_4O$, are formed, both of which crystallize in monosymmetric forms; the one melts at 47°, and the other, which is also a product of the action of phosphorus pentachloride on phthalide, at 88°. Theory, indeed, allows the formation of two isomeric tetrachlorides:





The compounds in question, however, exhibit an identical chemical behaviour. On heating with concentrated sulphuric acid, or on boiling with alcoholic potash, they are converted into phthalic acid, and phenol combines with them to form the phenyl ether mentioned above. These facts seem to indicate a case of physical isomerism, but all endeavours to convert either of the compounds into the other have proved unsuccessful (v. Gerichten).

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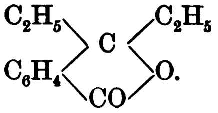
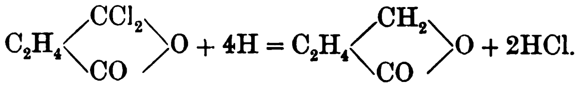
[1] Gräbe and Guye, *Ber. Deutsch. Chem. Ges.* xvii. 2851.
[2] Gräbe, *Ber. Deutsch. Chem. Ges.* xvi. 860.
[3] Schreder, *ibid.* vii. 705; v. Gerichten, *ibid.* xiii. 419.

According to Claus and Hoch, the tetrachloride, which melts at 88° and boils at about 274°, is alone obtained and is best prepared by heating for 15 hours at 245°. Carbonyl chloride and orthochlorobenzoyl chloride are also formed in the reaction.[1]

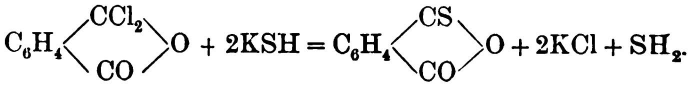
A compound is formed by the action of zinc ethyl on phthalyl chloride, which is looked upon by Wischin as *phenylenediethylacetone*, $C_6H_4(CO.C_2H_5)_2$. It separates from ethereal solution in splendid crystals, which possess a pleasant, fruity smell, and melt at 52°. Wischin was, however, unable to obtain a compound of it with acid sodium sulphite, and V. Meyer has shown that it is not a ketone, since it does not form a hydroxylamine compound.[2] The constitution of this compound can readily be explained in accordance with the present views in regard to phthalyl chloride, and is as follows :



Succinyl chloride (Part II., p. 191) has obviously an analogous constitution to phthalyl chloride, and its reduction to the anhydride or lactone of γ-hydroxybutyric acid (Part. II., p. 169) thus receives a simple explanation :



Phthalyl sulphide or *Thiophthalic anhydride*, $C_8H_4O_2S$, is formed by the action of potassium hydrosulphide on phthalyl chloride[3] or its phenyl ether :[4]



It crystallizes from alcohol in small plates or needles. melts at 114° and boils at 284°.

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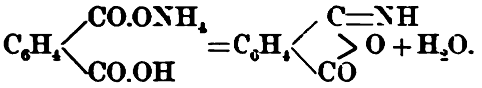
[1] *Ber. Deutsch. Chem. Ges.* xix. 1187.

[2] *Ibid.* xvii. 817.

[3] Schreder, *ibid.* vii. 705.

[4] Gräbe and Zschokke, *ibid.* xvii. 1175.

2243 *Phthalimide*, $C_8H_4O_2(NH)$, is obtained by heating acid ammonium phthalate :[1]



$$C_6H_4\left\langle\begin{array}{l}CO.ONH_4\\CO.OH\end{array}\right. = C_6H_4\left\langle\begin{array}{l}C{=}NH\\CO\end{array}\right\rangle O + H_2O.$$

It is also formed by the action of ammonia on the anhydride, chloride,[2] or sulphide,[3] as well as by heating phthalic acid with ammonium or potassium thiocyanates.[4] It is insoluble in cold water, slightly soluble on boiling, and crystallizes from ether in six-sided prisms, which melt at 228°[5] and sublime in small plates. It is decomposed on heating with slaked lime into carbon dioxide and benzonitril,[6] and is reduced to phthalimidine (p. 444) by tin and hydrochloric acid.

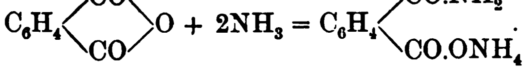
When phthalimide is heated with aniline or one of its homologues, ammonia is evolved and the corresponding substituted phthalimide formed. If a phenol be substituted for the amine, ammonia is also evolved, and a substance belonging to the class of phthaleïns is produced.

These bodies are identical with those prepared from phthalic anhydride.[7]

Potassium phthalimide, $C_8H_4O_2(NK)$, is obtained in white plates by adding alcoholic potash to an alcoholic solution of phthalimide (Cohn).

Silver phthalimide, $C_8H_4O_2(NAg)$, is formed as a heavy, white precipitate when silver nitrate is added to an aqueous solution of the potassium salt, or when an alcoholic solution of phthalimide is treated with an ammoniacal silver solution (Laurent).

Phthalamic acid, $C_6H_4(CO.NH_2)CO_2H$. Marignac prepared the ammonium salt of this acid by dissolving anhydrous naphthalic acid (phthalic acid) in ammonia, and named it *naphthalamide*.[8] It was also obtained by Laurent, who added ammonia to a hot, alcoholic solution of the anhydride :[9]



$$C_6H_4\left\langle\begin{array}{l}CO\\CO\end{array}\right\rangle O + 2NH_3 = C_6H_4\left\langle\begin{array}{l}CO.NH_2\\CO.ONH_4\end{array}\right. .$$

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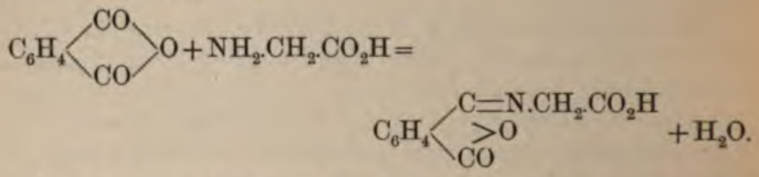
[1] Laurent, *Ann. Chem. Pharm.* xli. 110.
[2] Kuhara, *Amer. Chem. Journ.* iii. 26.
[3] Gräbe and Zschokke, *loc. cit.*
[4] Ossian Aschan, *Ber. Deutsch. Chem. Ges.* xix. 1398.
[5] Cohn, *Ann. Chem. Pharm.* ccv. 301.
[6] Laurent, *Jahresb Chem.* 1868, 549.
[7] Hall, Private Communication.
[8] *Ann. Chem Pharm.* xlii. 219.
[9] *Ann. Chim. Phys.* [3] xxiii. 117.

The barium salt is formed when phthalimide is boiled with baryta water (Kuhara), and the potassium salt by the continued boiling of potassium phthalimide with water.[1] It may be more simply prepared by the action of 25 per cent. caustic potash solution on phthalimide.[2] When concentrated hydrochloric acid is added to the solution, the phthalamic acid is gradually deposited in short, well developed, transparent prisms, which melt at 148°—149° and decompose at a slightly higher temperature into water and phthalimide. It has an acid taste, is tolerably soluble in cold water and is gradually converted by it into acid ammonium phthalate, the change taking place rapidly on boiling (Aschan).

Ethyl phthalimide, $C_6H_4O_2(NC_2H_5)$, is prepared by the distillation of phthalic anhydride with aqueous ethylamine; it crystallizes in needles or prisms, melts at 78·5° and boils at 276°—278°.[4]

Acetphthalimide, $C_8H_4O_2(NCO.CH_3)$, is formed by heating phthalimide with acetic anhydride for some time. It crystallizes in large octohedra and is decomposed by boiling water or by alkalis in the cold into acetic acid and phthalimide.[5]

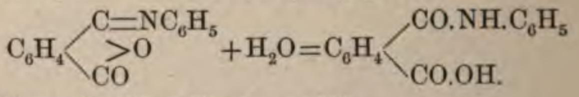
Phthaluric acid is obtained by heating phthalic anhydride with amido-acetic acid:



$$C_6H_4\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle O + NH_2.CH_2.CO_2H = C_6H_4\left\langle\begin{matrix}C{=}N.CH_2.CO_2H\\ >O\\ CO\end{matrix}\right. + H_2O.$$

It crystallizes from hot water in long, thin needles, which melt at 191°—192°, and are decomposed on boiling with concentrated hydrochloric acid into phthalic and amido-acetic acids.[6]

Phenylphthalimide or *Phthalanil*, $C_8H_4O_2(NC_6H_5)$, is prepared by distilling phthalic acid with aniline; it crystallizes from alcohol in needles, which melt at 205°, but sublime at a lower temperature.[7] On boiling with ammonia and alcohol, it is converted into *phthalanilic acid*, or phenylphthalamic acid:



$$C_6H_4\left\langle\begin{matrix}C{=}NC_6H_5\\ >O\\ CO\end{matrix}\right. + H_2O = C_6H_4\left\langle\begin{matrix}CO.NH.C_6H_5\\ CO.OH.\end{matrix}\right.$$

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[1] Landsberg, *Ann. Chem. Pharm.* ccxv. 198.

[2] Ossian Aschan, *Ber. Deutsch. Chem. Ges.* xix. 1401.

[3] Michael, *ibid.* x. 1646.

[4] Wallach and Kamenski, *ibid.* xiv. 171.

[5] Ossian Aschan, *ibid.* xix. 1400.

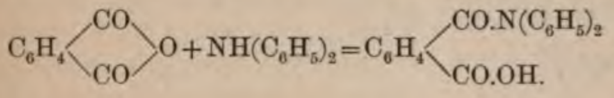
[6] Drechsel, *Journ. Prakt. Chem.* [2] ccxxvii. 418.

[7] Gerhardt and Laurent, *Ann. Chem. Phys.* [2] xxiv. 189; Döbner, *Ann. Chem. Pharm.* ccx. 267.

This substance crystallizes from hot water or alcohol in small plates, which melt at 192° and decompose into water and phthalanil at a higher temperature.

Analogous compounds are obtained from the substitution products of aniline[1] and its homologues,[2] from the amidophenols,[3] and from the amidobenzoic acids.[4]

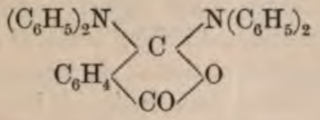
Diphenylphthalamic acid is formed when equal molecules of phthalic anhydride and diphenylamine are heated together:



$$C_6H_4{<}\begin{array}{l}CO\\CO\end{array}{>}O + NH(C_6H_5)_2 = C_6H_4{<}\begin{array}{l}CO.N(C_6H_5)_2\\CO.OH.\end{array}$$

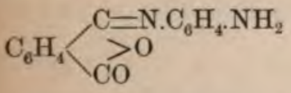
It is insoluble in water and crystallizes from alcohol in warty masses of small, lustrous prisms, which melt at 147°—148°.[5]

If two molecules of diphenylamine are employed, the so-called *diphenylphthaleïn* is formed; it is also obtained by the action of the base on phthalyl chloride,[6] and is tolerably soluble in alcohol, more readily in benzene, from which it crystallizes in large prisms, melting at 238°. It has the following constitution:

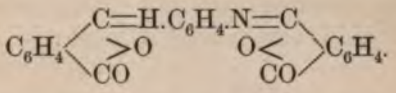


$$\begin{array}{c}(C_6H_5)_2N\searrow\quad\swarrow N(C_6H_5)_2\\ C\\ C_6H_4{<}\quad\quad{>}O\\ CO\end{array}$$

The aromatic diamines form two series of compounds with phthalic anhydride:[7]

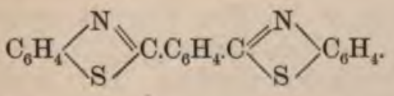


$$C_6H_4{<}\begin{array}{l}C{=}N.C_6H_4.NH_2\\ \;{>}O\\ CO\end{array}$$



$$C_6H_4{<}\begin{array}{l}C{=}H.C_6H_4.N{=}C\\ \;{>}O \qquad\qquad O{<}\\ CO \qquad\qquad\quad CO\end{array}{>}C_6H_4.$$

When orthamidothiophenol is heated with phthalic anhydride or phthalyl chloride, the compound $C_{20}H_{12}N_2S_2$ is formed, and probably has the following constitution:



$$C_6H_4{<}\begin{array}{l}N\\S\end{array}{>}C.C_6H_4.C{<}\begin{array}{l}N\\S\end{array}{>}C_6H_4.$$

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[1] Gabriel, *Ber. Deutsch. Chem. Ges.* xi. 2260; Fröhlich, *ibid.* xvii. 1801 and 2679.

[2] Michael, *ibid.* x. 579.

[3] Ladenburg, *ibid.* ix. 1528.

[4] Gabriel *loc. cit.*

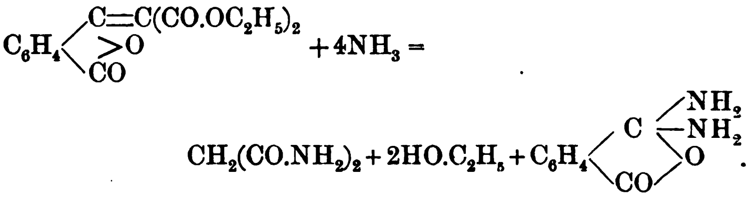
[5] Piutti, *Gaz. Chim. Ital.* xiii. 542; xiv. 470.

[6] Lellmann, *Ber. Deutsch. Chem. Ges.* xv. 830.

[7] Biedermann, *ibid.* x. 1160.

It crystallizes from alcohol in thin needles or thick prisms, which melt at 112°; it is a weak base and forms a hydrochloride which is only slightly soluble and crystallizes well, but is readily decomposed by water.[1]

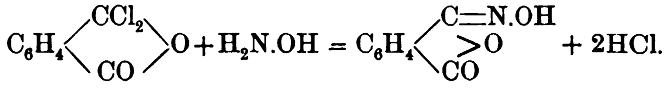
2244 *Phthalyldiamide.* Phthalylmalonic ether is formed by the action of phthalyl chloride on sodmalonic ether, and reacts with ammonia to form malonamide, alcohol and phthalyldiamide:[2]



$$C_6H_4\left<\begin{array}{l}C{=}C(CO.OC_2H_5)_2\\ \quad>O\\ CO\end{array}\right. + 4NH_3 = CH_2(CO.NH_2)_2 + 2HO.C_2H_5 + C_6H_4\left<\begin{array}{l}C\begin{array}{l}\diagup NH_2\\ -NH_2\end{array}\\ \qquad >O\\ CO\diagup\end{array}\right. .$$

This body may also be obtained in a similar manner from phthalylaceto-acetic ether,[3] and by allowing phthalimide to stand for some hours in contact with concentrated ammonia.[4] It forms a glittering powder, consisting of microscopic, very refractive rhombohedra, only slightly soluble in water and alcohol, and is decomposed into ammonia and phthalimide when heated with either of these. It fuses at 219°—220°, when carefully heated, forming a clear liquid, but ammonia is given off and the residue finally consists of phthalimide.

Phthalylhydroxylamine, $N(C_8H_4O_2)OH$, is formed when phthalyl chloride and sodium carbonate are alternately added to a concentrated solution of hydroxylamine hydrochloride, so that the liquid is always kept alkaline:



$$C_6H_4\left<\begin{array}{l}CCl_2\diagdown\\ \qquad\quad >O\\ CO\diagup\end{array}\right. + H_2N.OH = C_6H_4\left<\begin{array}{l}C{=}N.OH\\ \quad>O\\ CO\end{array}\right. + 2HCl.$$

It is insoluble in ether, but dissolves slightly in water, more readily in boiling alcohol, from which it crystallizes in small plates or needles, which, after drying, form a yellow powder, melting at 230° with decomposition. It is an acid, decomposes carbonates and forms a red solution in alkalis. Alcoholic potash added to its solution in alcohol precipitates the potassium salt, $N(C_8H_4O_2)OK$, which consists, as does the sodium compound, of an amorphous red powder. The silver compound is obtained by double decomposition as a dark-red precipitate, the barium and lead salts being light red and yellowish red precipitates, while the copper salt, which is only thrown down from a concentrated solution, is green, and the aluminium and mercury salts are yellow.

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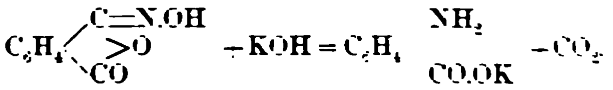
[1] Hofmann, *Ber. Deutsch. Chem. Ges.* 13, 1233.
[2] Wislicenus, *ibid.* xvii. Ref. 529.
[3] Bülow, *Ann. Chem. Pharm.* ccxxxvi. 188.
[4] Ossian Oschan, *Ber. Deutsch. Chem. Ges.* xix. 1398.

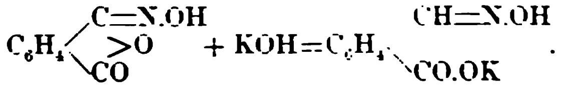
Ethylphthalylhydroxylamine, $N(C_8H_4O_2)OC_2H_5$, is obtained by treating the silver salt with ethyl iodide. It forms large crystals which melt at 103°—104° and boil at 27[illegible]°.

Phthalylhydroxylamine decomposes on dry distillation into phthalic anhydride, ammonia and nitrogen; a boiling solution of caustic potash resolves it into phthalic acid and hydroxylamine; while orthamidobenzoic acid is formed when it is heated in alcoholic solution with one molecule of potash:



$$C_6H_4\left\langle\begin{matrix}C{=}N.OH\\ >O\\ CO\end{matrix}\right. + KOH = C_6H_4\left\langle\begin{matrix}NH_2\\ \\ CO.OK\end{matrix}\right. + CO_2.$$

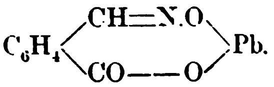
Hydroxyphthalamic acid is formed when an alcoholic solution of phthalylhydroxylamine is heated with potash for a short time:



$$C_6H_4\left\langle\begin{matrix}C{=}N.OH\\ >O\\ CO\end{matrix}\right. + KOH = C_6H_4\left\langle\begin{matrix}CH{=}N.OH\\ CO.OK\end{matrix}\right. .$$

Potassium hydroxyphthalamate separates out on cooling; it is readily soluble in water, and is deposited on evaporation in hard, yellow crystals.

The lead salt is thrown down when lead acetate is added to a solution of the potassium salt; it has the following constitution:

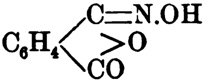


$$C_6H_4\left\langle\begin{matrix}CH{=}N.O\\ CO{-}{-}O\end{matrix}\right\rangle Pb.$$

When this is suspended in water and treated with sulphuretted hydrogen, a solution of the free acid is formed, which reddens litmus and, like that of the potassium salt, is coloured violet by ferric chloride. The solution of the acid decomposes gradually on standing, more rapidly when heated, with separation of phthalylhydroxylamine.

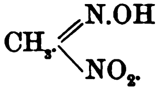
Phthalylhydroxylamine shows great similarity to the nitrolic acids, which, like the former, are colourless but are coloured red by the slightest trace of an alkali, and have a similar constitution:[1]

Phthalylhydroxylamine



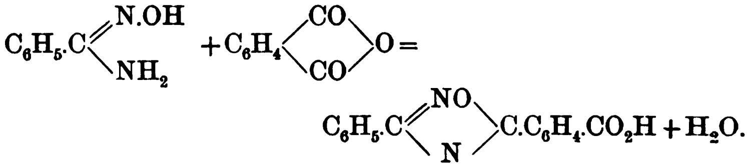
$$C_6H_4\begin{cases}C{=}N.OH\\ \quad >O\\ CO\end{cases}$$

Ethylnitrolic acid.



$$CH_3.C\begin{cases}N.OH\\ NO_2.\end{cases}$$

Benzenylazoximebenzenylcarboxylic acid, $C_{15}H_{10}N_2O_3$, is formed when phthalic anhydride is fused with benzenylamidoxime:

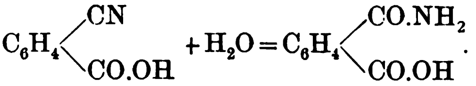


$$C_6H_5.C\begin{cases}N.OH\\ NH_2\end{cases} + C_6H_4\begin{cases}CO\\ CO\end{cases}>O =$$

$$C_6H_5.C\begin{cases}NO\\ N\end{cases}>C.C_6H_4.CO_2H + H_2O.$$

It crystallizes from hot alcohol in lustrous needles melting at 151°.[2]

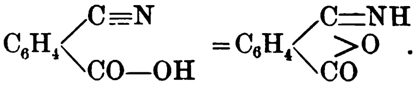
Orthocyanobenzoic acid, $C_6H_4(CN)CO_2H$, is obtained by adding orthodiazobenzoyl chloride to a hot solution of copper sulphate and cuprous cyanide; it is a thick, viscous liquid, which has not hitherto been prepared pure, since it readily changes into the isomeric phthalimide, phthalamic acid being probably formed as an intermediate product:



$$C_6H_4\begin{cases}CN\\ CO.OH\end{cases} + H_2O = C_6H_4\begin{cases}CO.NH_2\\ CO.OH\end{cases}.$$

This is then resolved into phthalimide and water.[3]

The conversion may however be simply explained by an intermolecular change:[4]



$$C_6H_4\begin{cases}C{\equiv}N\\ CO{-}OH\end{cases} = C_6H_4\begin{cases}C{=}NH\\ \quad >O\\ CO\end{cases}.$$

Ethyl orthocyanobenzoate, $C_6H_4(CN)CO_2.C_2H_5$, is prepared by diazotizing the ethyl ether of orthamidobenzoic acid and treating the product in the manner just described; it crystallizes in thick needles, melting at 70°.[5] It is gradually attacked when heated with hydroxylamine in alcoholic solution, *phthalimide-oxime* being formed:

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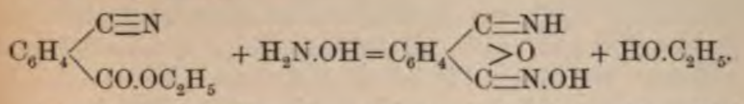
[1] Cohn, *Ann. Chem. Pharm.* ccv. 295.

[2] Schulz, *Ber. Deutsch. Chem. Ges.* xviii. 2463.

[3] Sandmeyer, *ibid.* xviii. 1496.

[4] Liebermann, *ibid.* xix. 2283.

[5] Müller, *ibid.* xix. 1491.



$$C_6H_4\left\langle\begin{matrix}C\equiv N\\ CO.OC_2H_5\end{matrix}\right. + H_2N.OH = C_6H_4\left\langle\begin{matrix}C=NH\\ >O\\ C=N.OH\end{matrix}\right. + HO.C_2H_5.$$

The latter crystallizes from dilute alcohol in needles, which melt at 250° and are converted into phthalimide by boiling with ferric chloride and hydrochloric acid.

ADDITION PRODUCTS OF PHTHALIC ACID.

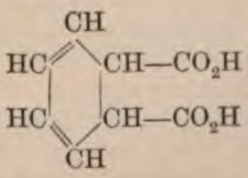
2245 *Dihydrophthalic acid*, $C_6H_6(CO_2H)_2$, is formed when a cold alkaline solution of phthalic acid is treated with sodium amalgam,[1] or better when the operation is carried on at the boiling point.[2] It crystallizes in hard, rhombic tablets, which are only slightly soluble in cold, more readily in hot water, and readily in alcohol. It is a strong dibasic acid; on heating with soda lime it decomposes into carbon dioxide, hydrogen and benzene, while the action of phosphorus pentachloride upon it yields hydrochloric acid, carbon dioxide, phosphorus oxychloride and benzoyl chloride. Bromine acts upon its aqueous solution in the following manner (Gräbe and Born):

$$C_6H_6(CO_2H)_2 + Br_2 = C_6H_5.CO_2H + CO_2 + HBr.$$

On heating with sulphuric or nitric acids, benzoic acid is also formed, together with phthalic acid, while ethyl benzoate, probably accompanied by ethyl formate, is produced when hydrochloric acid is passed into its alcoholic solution.

Hydrophthalic acid can be heated to 200° without undergoing any alteration; at a higher temperature, however, it decomposes with formation of phthalic anhydride.

All these reactions may be simply explained if we ascribe the following constitution to the acid:



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[1] Gräbe and Born, *Ann. Chem. Pharm.* cxlii. 330.
[2] Baeyer, *Ber. Deutsch. Chem. Ges.* xix. 1807.

Tetrahydrophthalic acid, $C_6H_8(CO_2H)_2$. The anhydride of this acid, $C_8H_8O_3$, is formed by the distillation of hydropyromellitic acid, $C_6H_6(CO_2H)_4$, and crystallizes from ether in hard, lustrous plates, which melt at 68° and sublime readily. It is insoluble in cold water, but dissolves in hot water with formation of the acid, which crystallizes in large plates, and is readily soluble in water, being, however, converted into the anhydride when the solution is heated to about 100°.[1]

Dibromotetrahydrophthalic acid, $C_6H_6Br_2(CO_2H)_2$, is obtained by the combination of dry bromine with dihydrophthalic acid, and crystallizes in rhombohedra (Baeyer).

Hexhydrophthalic acid, $C_6H_{10}(CO_2H)_2$, is formed when tetrahydrophthalic acid or dihydrophthalic acid[2] is heated to 230° with hydriodic acid, or when the former is treated with sodium amalgam and water, while dihydrophthalic acid is not attacked by these re-agents (Baeyer). It is slightly soluble in cold, somewhat more readily in hot water, and crystallizes in small prisms or plates, which melt at 203°—205° without forming an anhydride.

Bromomalophthalic acid, $C_6H_8Br(OH)(CO_2H)_2$, is prepared by adding bromine to an aqueous solution of tetrahydrophthalic acid, a dibromide being first formed, which is then decomposed by water:

$$C_6H_8Br_2(CO_2H)_2 + H_2O = C_6H_8Br(OH)(CO_2H)_2 + HBr.$$

It is readily soluble in water and crystallizes in small rhombic prisms or tablets. On heating with baryta water it is converted into the following compound.[3]

Tartrophthalic acid, $C_6H_8(OH)_2(CO_2H)_2$ is best obtained by dissolving the anhydride of tetrahydrophthalic acid in boiling water, and adding to one part of the anhydride rather more than an equal amount of bromine, the mixture being then heated on the water bath and treated with baryta water until the liquid has a permanent alkaline reaction. The barium salt is obtained on concentration in plates, from which the tartrophthalic acid is prepared by means of sulphuric acid. It crystallizes from a concentrated solution in colourless prisms containing two molecules of water, which are lost in a vacuum. On heating with hydriodic acid it is converted into hexhydrophthalic acid, the relation existing between these two bodies being similar to that between succinic and tartaric acids, while tetrahydrophthalic acid corresponds to fumaric acid.

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[1] Baeyer, *Ann. Chem. Pharm.* clxvi. 344.

[2] Mierski, *Ber. Deutsch. Chem. Ges.* iv. 558.

[3] Baeyer, *Ann. Chem. Pharm.* clxvi. 354.

HALOGEN SUBSTITUTION PRODUCTS OF PHTHALIC ACID.

2246 Chlorine does not act upon free phthalic acid, even in the presence of iodine; substitution takes place, however, when the gas is passed into an alkaline solution of the acid. Auerbach obtained in this way a monochlorophthalic acid, which crystallized from benzene in needles, melted at 149°—150°, was readily soluble in alcohol and remained on the evaporation of this solution as a syrup which gradually solidified. On heating, it yielded an anhydride boiling at 140°—143°.[1] Krüger obtained different results by oxidizing the two chloro-orthotoluic acids with potassium permanganate in faintly alkaline solution.[2]

v-Chlorophthalic acid, $C_6H_3Cl(CO_2H)_2(3:1:2)$, is also formed by the oxidation of the dichloronaphthalene melting at 107°, and crystallizes from hot water in stellate groups of silky needles, which melt at 184° and yield an anhydride which sublimes in long needles and melts at 122°—123°.[3]

a-Chlorophthalic acid (4 : 1 : 2) has also been prepared by the oxidation of ε-dichloronaphthalene[4] and by the action of phosphorus pentachloride on the corresponding sulphonic acid.[5] It is more readily soluble in water and alcohol than the v-acid, and crystallizes in silky needles, which melt at 130°—134° (Krüger) but according to Claus and Rée at 148°. It decomposes on distillation into water and the anhydride, which crystallizes in lustrous, asymmetric tablets, and melts at 96°—97°.

Dichlorophthalic acid, $C_6H_2Cl_2(CO_2H)_2$, is obtained by heating dichloronaphthalene tetrachloride, $C_{10}Cl_2H_6Cl_4$,[6] and β-dichloronaphthalene[7] with nitric acid. It is readily soluble in alcohol and hot water, and crystallizes in compact prisms, which melt at

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[1] *Jahresb. Chem.* 1880, 862.

[2] *Ber. Deutsch. Chem. Ges.* xviii. 1758.

[3] Guareschi, *ibid.* xix. 134.

[4] Alén, *Bull. Soc. Chem.* xxxvi. 434; Claus and Dehne, *Ber. Deutsch. Chem. Ges.* xv. 319; Claus and Müller, *ibid.* xviii. 3073.

[5] Rée, *ibid.* xviii. 3359; *Inaugurald. Bern.* 1886.

[6] Faust, *Ann. Chem. Pharm.* clx. 64.

[7] Atterberg, *Ber. Deutsch. Chem. Ges.* x. 574.

183°—185°. Its anhydride melts at 187° and forms crystals which are very similar to those of benzoic acid.

Trichlorophthalic acid, $C_6HCl_3(CO_2H)_2$, which has been prepared by the oxidation of β-pentachloronaphthalene with nitric acid, forms a yellowish, crystalline mass, and is converted on heating into the anhydride which melts at 157° and sublimes in long needles.[1]

Tetrachlorophthalic acid, $CCl_4(CO_2H)_2$. was obtained from a-pentachloronaphthalene. It is also formed by the action of chlorine on phthalic acid in presence of antimony chloride,[2] and crystallizes from water in small plates or hard, thick prisms, which melt at 250° and form an anhydride, which crystallizes in long needles, melting at 245°; these are insoluble in cold water but gradually dissolve in hot water, the acid being re-formed.[3]

Ethyl tetrachlorophthalate, $C_6Cl_4(CO_2C_2H_5)_2$, is prepared by heating the silver salt with ethyl iodide; it forms large prisms which melt at 60°. An isomeric compound is obtained when the acid is treated with phosphorus chloride and the tetrachlorophthalyl chloride formed submitted to the action of sodium ethylate (p. 461); it crystallizes in tablets and melts at 124°.[4]

v-Bromophthalic acid, $C_6H_3Br(CO_2H)_2$ (3 : 1 : 2), is formed when phthalic acid is heated with bromine and water to 180°; it is an indistinctly crystalline powder which melts at 138°—140° and yields an anhydride melting at 60°—65°.[5]

a-Bromophthalic acid (4 : 1 : 2) is obtained by the oxidation of bromonitronaphthalene, $C_{10}H_6Br(NO_2)$,[6] tetrabromo-β-naphthol[7] and dibromamidonaphthalene[8] with potassium permanganate. It crystallizes in white, prismatic needles, which melt at 175°—176° and are converted into an anhydride melting at 131°—132°.

a-Dibromophthalic acid, $C_6H_2Br_2(CO_2H)_2$ (3 : 6 : 1 : 2), was prepared by Guareschi by the oxidation of a-dibromonaphthalene with nitric acid. It separates from hot water as a crystalline powder, which melts at about 135° with decomposition; on further heating the anhydride sublimes in light, nacreous needles melting at 207·5°—208°.

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[1] Atterberg and Widmann, *Ber. Deutsch. Chem. Ges.* x. 1843.

[2] *Ibid.* xviii. Ref. 676.

[3] Gräbe, *Ann. Chem. Pharm.* cxlix. 18.

[4] Gräbe, *Ber. Deutsch. Chem. Ges.* xvi. 860.

[5] Faust, *Ann. Chem. Pharm.* clx. 62; Pechmann, *Ber. Deutsch. Chem. Ges.* xii. 2126.

[6] Guareschi, *Ann. Chem. Pharm.* ccxxii. 262.

[7] A. J. Smith. *Journ. Chem. Soc.* 1879, i. 792.

[8] Meldola, *ibid.* 1885, i. 511; see also Stallard, *ibid.* 1886, i. 187.

β-Dibromophthalic acid is formed by the oxidation of pentabromo-*α*-naphthol, and crystallizes from hot water in needles which melt at 206° and are thus converted into the anhydride, which sublimes in long needles and melts at 208°. The salts of this acid are, with the exception of those of the alkali metals, only slightly soluble in water.[1]

Tribromophthalic acid, $C_6HBr_3(CO_2H)_2$, is prepared from pentabromo-*β*-naphthol; it is almost insoluble in cold water and crystallizes from hot water in lustrous plates which melt at 190°—191° and are converted at a higher temperature into the anhydride, which sublimes in white plates and melts at 157°.[2]

Tetrabromophthalic acid, $C_6Br_4(CO_2H)_2$, was obtained by Blümlein as a product of the oxidation of tetrabromorthoxylene; it is almost insoluble in the ordinary solvents, and crystallizes from boiling water in lustrous needles, and on the evaporation of its solution in benzene in prisms, which melt at 266° and are thus converted into the anhydride, which sublimes in small, lustrous needles, melting at 258°—259°. Its salts are for the most part insoluble, or only slightly soluble, in water.

NITROPHTHALIC ACIDS.

2247 *v-Nitrophthalic acid*, $C_6H_3(NO_2)(CO_2H)_2$ (3 : 2 : 1), is formed by the continued boiling of naphthalene with nitric acid,[3] by the action of a mixture of nitric and sulphuric acids on phthalic acid[4] and by the oxidation *α*-nitronaphthalene with potassium permanganate[5] or of *α*-dinitronaphthalene with nitric acid.[6] In order to prepare it, one part of nitronaphthalene is dissolved in 7 parts of 90 per cent. acetic acid, and to this are gradually added 5 parts of chromium trioxide; water is then added and the solution extracted with chloroform to remove the orthonitrophthalide which is always formed. The acid liquid is then treated with barium carbonate, and the insoluble barium nitrophthalate decomposed by carbonate of soda. The solution of the sodium salt is then acidified and the nitrophthalic acid extracted with ether.[1] It crystallizes from this in light yellow, monoclinic prisms, which are slightly soluble in cold, more freely in hot water, and readily in alcohol. It decomposes on heating into water and the anhydride; in a small sealed tube it melts at 218° (Miller).

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[1] Blümlein, *Ber. Deutsch. Chem. Ges.* xvii. 2485.
[2] Flessa, *ibid.* xvii. 1479.
[3] Laurent, *Ann. Chem. Pharm.* xli. 110; Marignac, *ibid.* xlii. 7.
[4] Faust, *ibid.* clx. 57.
[5] Guareschi, *Ber. Deutsch. Chem. Ges.* x. 294.
[6] Aguiar, *ibid.* v. 899.

Acid ethyl v-nitrophthalate, $C_6H_3(NO_2)(CO_2C_2H_5)CO_2H$, is obtained by passing hydrochloric acid into an alcoholic solution of the acid; it crystallizes from hot water in long needles, melting at 110·5°.

Normal ethyl v-nitrophthalate, $C_6H_3(NO_2)(CO_2C_2H_5)_2$, is prepared from the silver salt by the action of ethyl iodide, and crystallizes from alcohol in long, rhombic prisms, melting at 45° (Miller).

a-Nitrophthalic acid, $C_6H_3(NO_2)(CO_2H)_2+H_2O$ (4 : 2 : 1), is formed, together with the preceding compound, by the nitration of phthalic acid.[2] In order to prepare it, 50 grms. of phthalic acid are heated with 75 grms of sulphuric acid and the same amount of fuming nitric acid for two hours on the water bath; 120 grms. of water are then added, and the whole allowed to stand for twelve hours in the cold. The precipitate is washed and extracted with ether, the residue after the evaporation of this consisting of a mixture of the two acids accompanied by a little picric acid. It is re-crystallized from water, to remove the greater portion of the v-acid, the mother liquor evaporated to dryness, and the residue dissolved in alcohol and treated with hydrochloric acid gas, which converts the v-acid into the acid and the a-acid into the normal ether. These are separated by carbonate of soda solution, and the normal ether then converted into the potassium salt by the action of alcoholic potash; this is then acidified with hydrochloric acid and the free acid extracted with ether. It may be still more easily obtained by heating paranitrophthalide with dilute nitric acid to 140°.[3] It crystallizes in small needles, which are readily soluble in water and alcohol, effloresce in the air, lose their water at 100°, and then melt at 161°.

Acid ethyl a-nitrophthalate, $C_6H_3(NO_2)(CO_2.C_2H_5)CO_2H$, is formed in small quantity when an alcoholic solution of the acid is treated for a short time with hydrochloric acid, and crystallizes from water, in long, thin needles, which melt at 127°—128°.

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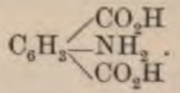
[1] Beilstein and Kurbatow, *Ann. Chem. Pharm.* ccii. 217.
[2] Miller, *ibid.* ccviii. 223.
[3] Hönig, *Ber. Deutsch. Chem. Ges.* xvii. 3447.

Normal ethyl a-nitrophthalate, $C_6H_3(NO_2)(CO_2.C_2H_5)_2$, is insoluble in water and crystallizes from alcohol in lustrous tablets, which melt at 34°.

a-Nitrophthalic anhydride, $C_8H_3(NO_2)O_3$, is obtained by heating the acid to 170° and subliming the residue in a current of air at 210°, in the form of fascicular crystals, which melt at 114° and are readily soluble in ether and hot water. If the aqueous solution be evaporated, a-nitrophthalic acid is deposited.

Dinitrophthalic acid, $C_6H_2(NO_2)_2(CO_2H)_2$ (5 : 3 : 2 : 1), is formed when β-dinitrophthalene is heated to 150° with nitric acid of sp. gr. 1·15 in a sealed tube, small quantities of nitrophthalic acid, s-dinitrobenzoic acid, and picric acid being also formed. It crystallizes in large prisms, which are readily soluble in water and alcohol, and melt at 226°.[1]

AMIDOPHTHALIC ACIDS,



$$C_6H_3\begin{cases}CO_2H\\NH_2\\CO_2H\end{cases}.$$

2248 *v-Amidophthalic acid.* When the v-nitro-acid is treated with tin and hydrochloric acid in the cold, needles of the compound $C_6H_3(NH_2.ClH)(CO_2H)_2+SnCl_2+2H_2O$ are formed. If the hydrochloric acid solution of this be treated with sulphuretted hydrogen and evaporated, carbon dioxide is given off and meta-amidobenzoic acid formed.

Ethyl v-amidophthalate, $C_6H_3(NH_2)(CO_2.C_2H_5)_2$, is prepared by treating a well-cooled alcoholic solution of the ether of the nitro-acid with hydrochloric acid and zinc dust. It is a yellow liquid, which decomposes on heating and forms a splendid blue fluorescent solution in ether (Miller).

a-Amidophthalic acid. When the a-nitro-acid is reduced, no carbon dioxide is evolved, but no double tin salt is formed. On removing the tin and evaporating, however, carbon dioxide is evolved just as in the case of the v-acid, and metamidobenzoic acid formed.

If the reduction be carried on by means of zinc dust and acetic acid, a double compound of zinc acetate and zinc amidophenate is formed, which has probably the constitution $C_6H_3(NH_2)(CO_2H)CO_2.Zn.O.CO.CH_3$, and crystallizes in fine, white needles, which form an almost colourless solution in hot water, while its solution in acetic acid is coloured yellow and has a green fluorescence. It dissolves in caustic soda, but the solution decomposes on heating, zinc carbonate is deposited and the amidophthalic acid decomposed.[1]

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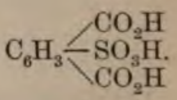
[1] Beilstein and Kurbatow, *Ann. Chem. Pharm.* ccii. 224.

Ethyl a-amidophthalate was first prepared by Baeyer but mistaken for the v-compound[2] until Miller showed that it is derived from the a-acid.[3] This substance is obtained in a similar manner to the isomeric compound; it is insoluble in water, slightly soluble in dilute acid, readily in alcohol, from which it crystallizes in monoclinic prisms, which melt at 95°; the dilute ethereal solution shows a faint blue fluorescence.

SULPHOPHTHALIC ACIDS,



$C_6H_3\begin{cases}CO_2H\\SO_3H.\\CO_2H\end{cases}$

2249 *a-Sulphophthalic acid* (1 : 4 : 2) is obtained by heating phthalic acid or phthalic anhydride with strong, fuming sulphuric acid,[4] and by the oxidation of β-naphthalenesulphamide, $C_{10}H_7SO_2.NH_2$, and dinitronaphtholsulphonic acid, $C_{10}H_4(NO_2)_2(OH)SO_3H$.[5] It remains as a syrup when its solution is evaporated on the water bath, but solidifies after heating for some time to a mass consisting of stellate groups of sharply pointed prisms; these contain a molecule of water, which is lost at 140°, a brownish syrup being formed, which often solidifies on standing. On heating to 180°, the anhydride, $C_6H_3(C_2O_3)SO_3H$, is formed as a hard, brown, very hygroscopic mass.

The normal barium salt crystallizes in plates or silky needles, slightly soluble in water; when it is dissolved in the necessary amount of hydrochloric acid, the monacid salt, $C_6H_3(CO_2BaSO_3)CO_2H+2H_2O$, is formed, and crystallizes from hot water in large needles; it is converted by solution in an excess of hydrochloric acid into the diacid salt, $(C_6H_3(CO_2H)_2SO_3)_2Ba+5H_2O$, which also crystallizes in lustrous needles.

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[1] Bernthsen and Semper, *Ber. Deutsch. Chem. Ges.* xix. 164.

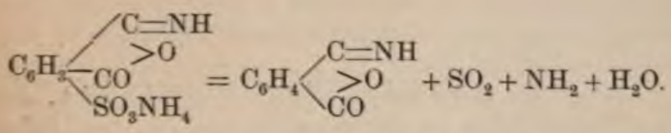
[2] *Ibid.* x. 124 and 1079.

[3] *Ibid.* xi. 1191.

[4] Löw, *Ann. Chem. Pharm.* cxliii. 249; Rée, *Ber. Deutsch. Chem. Ges.* xviii. 1629; *Inaugurald. Bern.* 1886; *Ann. Chem. Pharm.* ccxxxiii. 216.

[5] Gräbe, *Ber. Deutsch. Chem. Ges.* xviii. 1126.

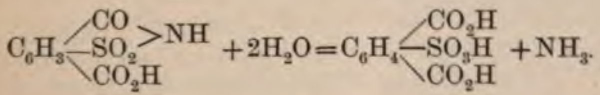
When the monacid ammonium salt is heated, the ammonium salt of *a-sulphophthalimide* is formed; it crystallizes in monosymmetric prisms, and is decomposed on heating with formation of phthalimide:



$$C_6H_3\begin{array}{l}\diagup C{=}NH\\ \quad >O\\ -CO\\ \diagdown SO_3NH_4\end{array} = C_6H_4\begin{array}{l}\diagup C{=}NH\\ \quad >O\\ \diagdown CO\end{array} + SO_2 + NH_2 + H_2O.$$

a-Sulphamidophthalic acid, $C_6H_3(SO_3.NH_2)(CO_2H)_2$. When a-sulphophthalic anhydride is treated with phosphorus pentachloride, the monochloride, $C_6H_3(SO_2Cl)(CO_2H)_2$, is formed, and is converted by ammonia into the amide, which crystallizes from water in small, transparent prisms (Rée).

v-Sulphophthalic acid (1 : 3 : 2) is formed when *a*-naphthalenesulphamide is oxidized with potassium permanganate. The first product is the anhydride of sulphamidophthalic acid, which yields the sulphonic acid on heating with hydrochloric acid:



$$C_6H_3\begin{array}{l}\diagup CO\\ -SO_2\\ \diagdown CO_2H\end{array}\!\!>NH + 2H_2O = C_6H_4\begin{array}{l}\diagup CO_2H\\ -SO_3H\\ \diagdown CO_2H\end{array} + NH_3.$$

It is readily soluble in water, and forms salts which crystallize well.[1] The normal barium salt, $(C_6H_3(CO_2)_2Ba.SO_3)_2Ba+8H_2O$, crystallizes in transparent tablets.

Sulphamidophthalic anhydride or *Sulphinidephthalic acid*, $C_8H_5NSO_3 + 2H_2O$, crystallizes from hot water in needles, which become anhydrous at 155.° Alkalis do not convert it into sulphamicphthalic acid; it is a dibasic acid, the hydrogen of the imide-group being easily replaced by metals.

Normal potassium sulphinidephthalate, $C_8H_3K_2NSO_3$, is very readily soluble in water and dries to an elastic mass, from which semi-crystalline, spherical masses separate on standing.

Acid potassium sulphinidephthalate, $C_8H_4KNSO_3 + H_2O$, is only slightly soluble in cold, readily in hot water, and crystallizes in long acute prisms, which rapidly lose their water at 100°.

Normal silver sulphinidephthalate, $C_8H_3Ag_2NSO_3 + H_2O$, is a white precipitate, which is scarcely soluble in boiling water, but dissolves in a hot solution of potassium nitrate and separates out again on cooling.

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[1] Remsen and Comstock, *Amer. Chem. Journ.* v. 106; Stokes, ibid. vi. 262.

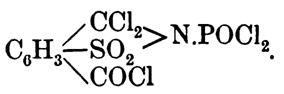
Acid silver sulphinidephthalate, $C_8H_4AgNSO_3 + H_2O$, is formed when the normal salt is heated with nitric acid, or when silver nitrate is added to a dilute boiling solution of the acid potassium salt. It crystallizes on cooling in long, pliant needles, which become anhydrous below 135°.

The silver salt is converted into the methyl ether by treatment with methyl iodide.

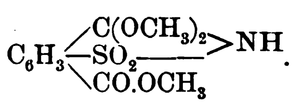
Normal methyl sulphinidephthalate, $C_8H_3(CH_3)_2NSO_3$, crystallizes from alcohol in colourless needles, which melt at 180° and readily sublime in iridescent plates.

Acid methyl sulphinidephthalate, $C_8H_4(CH_3)NSO_3$, separates from an alcoholic or hot aqueous solution in long, striated prisms, or long, narrow tablets, which melt at 190·7°—191·7° and readily volatilize. When it is successively treated with phosphorus trichloride and methyl alcohol the dimethyl ether is formed.

In order to determine the constitution of the acid sulphinidephthalates, the acid potassium salt was heated with phosphorus pentachloride, the compound $C_8H_3Cl_3SO_2NPOCl_2$ being formed; it crystallizes in small prisms, and is converted by methyl alcohol into the trimethyl ether, $C_8H_4(CH_3)_3NSO_6$, which separates from hot water in needles or long narrow prisms, which melt at 140·5°—141·5°. The constitution of these compounds is expressed by the following formulæ:

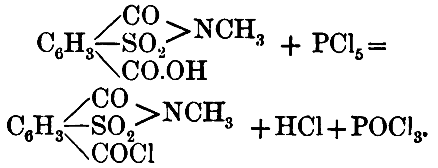


$$C_6H_3\left\langle\begin{matrix}CCl_2 \\ SO_2 \\ COCl\end{matrix}\right. \!>N.POCl_2.$$

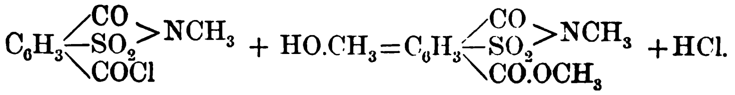


$$C_6H_3\left\langle\begin{matrix}C(OCH_3)_2 \\ SO_2 \\ CO.OCH_3\end{matrix}\right. \!>NH.$$

Since the monomethyl ether is converted into the diethyl ether by the action of phosphorus chloride for a short time, followed by the treatment described above, it follows that in the first of these, and therefore in the acid sulphinidephthalates, it is the hydrogen of the imido-group which is replaced (Stokes):



$$C_6H_3\left\langle\begin{matrix}CO \\ SO_2 \\ CO.OH\end{matrix}\right. \!>NCH_3 + PCl_5 = C_6H_3\left\langle\begin{matrix}CO \\ SO_2 \\ COCl\end{matrix}\right. \!>NCH_3 + HCl + POCl_3.$$



$$C_6H_3\left\langle\begin{matrix}CO \\ SO_2 \\ COCl\end{matrix}\right. \!>NCH_3 + HO.CH_3 = C_6H_3\left\langle\begin{matrix}CO \\ SO_2 \\ CO.OCH_3\end{matrix}\right. \!>NCH_3 + HCl.$$

ISOPHTHALIC ACID OR METAPHTHALIC ACID.

2250 This compound is formed by the oxidation of metaxylene,[1] metatoluic acid,[2] and other meta-compounds with two side-chains containing carbon. It has also been obtained by fusing potassium metasulphobenzoate[3] and potassium metabromobenzoate[4] with sodium formate (Part III. p. 31), and has been found among the products of the oxidation of colophony with nitric acid.[5] In order to prepare it, metaxylene is converted into metaxylylene diethyl ether, and this is then oxidized with chromic acid solution, the reaction proceeding very smoothly.[6] It dissolves in 7,800 parts of water at 25° and in 460 parts at 100°, crystallizing in hair-like needles, which usually extend through the whole liquid, and are readily soluble in alcohol.[7] It melts at above 300° and sublimes without decomposition.

Potassium isophthalate, $C_8H_4O_4K_2$, is readily soluble in water, less readily in alcohol, from which it crystallizes in fascicular groups of needles.

Calcium isophthalate, $2C_8H_4O_4Ca + 5H_2O$, is scarcely more soluble in hot than in cold water and forms fine needles.

Barium isophthalate, $2C_8H_4O_4Ba + 7H_2O$, is readily soluble in water and crystallizes from a concentrated solution in lustrous needles, which effloresce in the air.[8]

Silver isophthalate, $C_8H_4O_4Ag_2$, is an amorphous precipitate, which, like mercury thiocyanate, forms a voluminous vermiform mass on heating.

Methyl isophthalate, $C_6H_4(CO_2.CH_3)_2$, has been prepared from the silver salt by means of methyl iodide. It crystallizes from dilute alcohol in long fine needles, melts at 64°—65°, and distils without decomposition.[9]

Ethyl isophthalate, $C_6H_4(CO_2.C_2H_5)_2$, has been obtained by the action of hydrochloric acid on an alcoholic solution of the acid.

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[1] Fittig and Velguth, *Ann. Chem. Pharm.* cxlviii. 11.
[2] Weith and Landolt, *Ber. Deutsch. Chem. Ges.* viii. 721.
[3] V. Meyer, *Ann. Chem. Pharm.* clvi. 275.
[4] Ador and Meyer, *ibid.* clix. 16.
[5] Fittig and Storss, *ibid.* cliii. 284.
[6] W. H. Perkin, jun. Private communication.
[7] Fittig and Storss, *Ann. Chem. Pharm.* cliii. 284.
[8] Kelbe, *ibid.* ccx. 20.
[9] V. Meyer, *Ber. Deutsch. Chem. Ges.* iv. 262; Baeyer, *Ann. Chem. Pharm.* clxvi. 340.

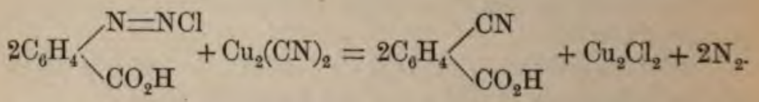
It is a liquid which possesses a faint but pleasant odour, boils at about 285°, and solidifies at 0° to a dazzling white, radiating mass (Fittig and Storss).

Phenyl isophthalate, $C_6H_4(CO_2.C_6H_5)_2$, is formed when phenol is heated with the chloride; it crystallizes in long, fine needles which melt at 120° and are only slightly soluble in alcohol.[1]

Isophthalyl chloride, $C_6H_4(COCl)_2$, is obtained by the distillation of the acid with phosphorus chloride as an oily liquid, which boils at 276° and solidifies to a radiating, crystalline mass, melting at 41° (Schreder).

Isophthalamide, $C_6H_4(CO.NH_2)_2$, is formed by the action of ammonia on the chloride and is a light, white powder, which melts at 265°, is slightly soluble in alcohol, but scarcely dissolves in any other of the ordinary solvents. On heating with phosphorus pentoxide it is converted into isophthalonitril.[2]

Metacyanobenzoic acid, $C_6H_4(CN)CO_2H$, is obtained by allowing a hydrochloric acid solution of metadiazobenzoic acid to run into a solution of copper sulphate and cuprous cyanide:



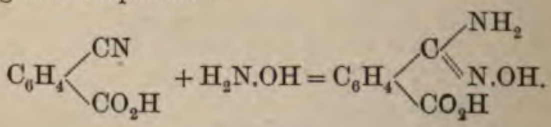
$$2C_6H_4\left<\begin{matrix}N{=}NCl\\CO_2H\end{matrix}\right. + Cu_2(CN)_2 = 2C_6H_4\left<\begin{matrix}CN\\CO_2H\end{matrix}\right. + Cu_2Cl_2 + 2N_2.$$

It is readily soluble in alcohol and hot water, and crystallizes from the latter in microscopic, arborescent needles, which after drying form a dull white powder and melt at 217°.

Boiling caustic soda solution readily converts it into isophthalic acid.[3]

Ethyl metacyanobenzoate, $C_6H_4(CN)CO.C_2H_5$, crystallizes in fine, matted needles, which melt at 48°.

Benzenylamidoximemetacarboxylic acid, is prepared by heating metacyanobenzoic acid for a long time with an alcoholic solution of hydroxylamine, and forms crystals which are readily soluble in alcohol and hot water, and melt at 200°. It is formed according to the equation:



$$C_6H_4\left<\begin{matrix}CN\\CO_2H\end{matrix}\right. + H_2N.OH = C_6H_4\left<\begin{matrix}C\left<\begin{matrix}NH_2\\N.OH\end{matrix}\right.\\CO_2H\end{matrix}\right.$$

---

[1] Schreder, *Ber. Deutsch. Chem. Ges.* vii. 708.

[2] Beyer, *Journ. Prakt. Chem.* [2] xxii. 351.

[3] Sandmeyer, *Ber. Deutsch. Chem. Ges.* xviii. 1496.

The ethyl ether is prepared in a similar manner from the corresponding ether of metacyanobenzoic acid and crystallizes from hot water in needles, which melt at 118°.[1]

Isophthalonitril, $C_6H_4(CN)_2$, is formed by the distillation of potassium benzenemetadisulphonate with potassium cyanide,[2] or of potassium metabromosulphonate with dehydrated potassium ferrocyanide;[3] it forms fine needles, which melt at 160°—161°, are only very slightly soluble in water, somewhat more readily in alcohol, and are converted into isophthalic acid by heating with alkalis.

ADDITION PRODUCTS OF ISOPHTHALIC ACID.

Tetrahydro-isophthalic acid, $C_6H_8(CO_2H)_2$, is prepared by boiling an alkaline solution of isophthalic acid with sodium amalgam for some time, and crystallizes from hot water in needles, which melt at 199°. Its dimethyl ether is an oily liquid.[4]

SUBSTITUTION PRODUCTS OF ISOPHTHALIC ACID.

2251 *Chloro-isophthalic acid*, $2C_6H_3Cl(CO_2H)_2 + H_2O$, has been obtained from the amido-acid by means of the diazo-reaction, and crystallizes from hot water in long, very fine needles, which become anhydrous at 120°, and melt at 278° (Beyer).

Iodo-isophthalic acid, $C_6H_3I(CO_2H)_2$ (4 : 3 : 1), is formed by the oxidation of acetyliodotoluene, $CH_3.CO.C_6H_3I.CH_3$, which will be subsequently described. It is scarcely soluble in cold, only very slightly in boiling water, and crystallizes from hot acetic acid in small, white needles, which melt at 203°—204°, but sublime in white, lustrous flocks, without previously melting, when carefully heated. On fusion with caustic potash, parahydroxybenzoic acid is formed, while it yields benzoic acid when reduced in alcoholic solution by sodium amalgam.[1]

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[1] Müller, *Ber. Deutsch. Chem. Ges.* xix. 1491.
[2] Barth and Senhofer, *ibid.* viii. 1481; *Ann. Chem. Pharm.* clxxiv. 235.
[3] Limpricht, *ibid.* clxxx. 92.
[4] Baeyer, *Ber. Deutsch. Chem. Ges.* xix. 1806.

Nitro-isophthalic acid, $2C_6H_3(NO_2)(CO_2H)_2+3H_2O$, is prepared by heating isophthalic acid with fuming nitric acid for some time; [2] it is slightly soluble in cold, very readily in boiling water and alcohol, and crystallizes in thin, lustrous plates, resembling those of benzoic acid, which readily lose their water and melt with slight decomposition at 248°—249°.

Its salts, some of which crystallize well, have been fully examined by Beyer.

Methyl nitro-isophthalate, $C_6H_3(NO_2)(CO_2.CH_3)_2$, is formed when hydrochloric acid is passed into an alcoholic solution of the acid, and crystallizes in fine, lustrous needles, which melt at 121·5°, and yield a vapour which smells like aniseed.

Ethyl nitro-isophthalate, $C_6H_3(NO_2)(CO_2.C_2H_5)_2$, forms fine needles or transparent prisms, which melt at 83·5°.

Amido-isophthalic acid, $C_6H_3(NH_2)(CO_2H)_2$, is readily obtained from the nitro-acid by reduction with tin and hydrochloric acid. It is only slightly soluble in cold water and alcohol, crystallizing from hot water in lustrous plates and from alcohol in prisms. It combines with acids and bases forming compounds which have been investigated by Beyer. Its ethers are obtained by the reduction of the corresponding nitro-compounds.

Methyl amido-isophthalate, $C_6H_3(NH_2)(CO_2.CH_3)_2$, crystallizes from wood-spirit in thin, yellowish plates or tablets, which melt at 176°.

Ethyl amido-isophthalate, $C_6H_3(NH_2)(CO_2.C_2H_5)_2$, forms thin plates or fascicular needles, melting at 118°. Its ethereal solution has a splendid violet fluorescence.

s-Sulpho-isophthalic acid, $CH_3(CO_2H)_2SO_3H+2H_2O$ (1 : 3 : 5), is prepared by the action of sulphur trioxide on isophthalic acid,[3] and by heating the latter to 200° with fuming sulphuric acid.[4] It is very readily soluble in water, but only slightly in dilute sulphuric acid, and crystallizes in long needles or transparent, four-sided, pointed, rhombic columns, which effloresce in dry air, but deliquesce in very damp air. The anhydrous acid melts at 257°—258°, a slight discolouration taking place.

a-Sulpho-isophthalic acid, $C_6H_3(CO_2H)_2SO_3H+2H_2O$ (1 : 3 : 4), is obtained by the oxidation of an alkaline solution of a-metaxylenesulphonic acid,[1] or metatoluylsulphamic acid[2] with potassium permanganate. It is readily soluble in water, and crystallizes from dilute sulphuric acid in flat, very hygroscopic needles melting at 235°—240°.

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[1] Klingel, *Ber. Deutsch. Chem. Ges.* xviii. 2701.

[2] Fittig and Storss, *ibid.* cliii. 285; Beyer, *Journ. Prakt. Chem.* [2] xxv. 465.

[3] Heine, *Ber. Deutsch. Chem. Ges.* xiii. 491.

[4] Lönnies, *ibid.* xiii. 703.

TEREPHTHALIC ACID.

2252 Paraphthalic acid is readily formed by the oxidation of those para-compounds which possess two side-chains containing carbon, such as paraxylene,[3] cymene, or methylpropylbenzene, $CH_3.C_6H_4.C_3H_7$, cuminol or cuminaldehyde, $COH.C_6H_4.C_3H_7$,[4] paratoluic acid,[5] &c. Caillot, as already mentioned, obtained it from oil of turpentine, $C_{10}H_{16}$, which is closely related to cymene. The isomerides of this, oil of cajeput, oil of citron, and the thymene contained in thymian, all yield terephthalic acid on oxidation,[6] and it is also formed when potassium parasulphobenzoate is fused with sodium formate.[7]

In order to prepare it, a mixture of 100 grms. of paraxylene, which need not be pure, 400 grms. of potassium dichromate and 550 grms. of sulphuric acid, diluted with two volumes of water, is heated for several days in a flask connected with a reflux condenser until the solution has become coloured a pure green; the unattacked xylene is then distilled off, and the solution filtered from the precipitated acid, which is dissolved in dilute carbonate of soda and precipitated by hydrochloric acid. The acid is obtained pure by repeating this process two or three times.

Cymene, which is easily prepared by distilling camphor with phosphorus pentoxide, may be employed instead of paraxylene, or Roman cumin oil, a mixture of cymene and cuminol, may be used.

Terephthalic acid is a tasteless powder, which appears crystalline under the microscope, is insoluble in ether and chloroform, and scarcely soluble in water and alcohol; the hot, saturated, aqueous solution has an acid reaction, and deposits the acid on

[1] Jacobsen and Lönnies, *Ber. Deutsch. Chem. Ges.* xiii. 1556.
[2] Coale and Remsen, *Amer. Chem. Journ.* iii. 214.
[3] Beilstein, *Ann. Chem. Pharm.* cxxxiii. 40.
[4] Müller and Warren de la Rue, *ibid.* cxxi. 87.
[5] Beilstein and Yssel de Schepper, *ibid.* cxxxvii. 308.
[6] Schwanert, *ibid.* cxxxii. 260.
[7] Remsen, *Ber. Deutsch. Chem. Ges.* v. 379.

cooling as an indistinctly crystalline powder. It sublimes when heated without previously melting.

Ammonium terephthalate, $C_8H_4O_4(NH_4)_2$, is deposited on the evaporation of its solution in small, lustrous crystals.

Calcium terephthalate, $C_8H_4O_4Ca + 3H_2O$, separates from hot water in small crystals, which dissolve in 1,214 parts of water at 6°.

Barium terephthalate, $C_8H_4O_4Ba + 4H_2O$, is deposited from a rapidly cooled solution as a white, granular powder; by gradual evaporation it is obtained in small, concentrically arranged tablets, which dissolve in 355 parts of water at 5°.

Silver terephthalate, $C_8H_4O_4Ag_2$, is an amorphous precipitate, which blackens in the light.

Methyl terephthalate, $C_8H_4O_4(CH_3)_2$, is formed by the action of the chloride on methyl alcohol,[1] and crystallizes from hot alcohol in large flat prisms, which melt at 140° and are volatile without decomposition. By means of this compound the smallest quantity of terephthalic acid can be detected. The substance is treated with phosphorus chloride and then with methyl alcohol, water being finally added and the methyl compound extracted with ether. On the evaporation of the latter characteristic crystals of the compound are obtained.

Ethyl terephthalate, $C_6H_4(CO_2.C_2H_5)_2$, forms white odourless prisms, which resemble those of urea and melt at 44°.

The following ethereal salts have been prepared by Beyer, some by means of the chloride, the remainder from the silver salt:[2]

	Melting-point.
Propyl terephthalate, $C_6H_4(CO_2.C_3H_7)_2$, long needles	31·0°
Isopropyl terephthalate, $C_6H_4(CO_2.C_3H_7)_2$, lustrous plates .	55·5°
Isobutyl terephthalate, $C_6H_4(CO_2.C_4H_9)_2$, needles.	52·5°

The normal butyl ether is liquid, while the tertiary butyl ether is only formed with great difficulty, and has not yet been obtained in considerable amount. Müller and Warren de la Rue have prepared the amyl ether; it crystallizes in scales, which are melted even by the warmth of the hand.

Phenyl terephthalate, $C_6H_4(CO_2.C_6H_5)_2$, crystallizes from alcohol in fine needles, melting at 191°.[3]

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[1] Warren de la Rue and Müller; Schwanert, *loc. cit.*

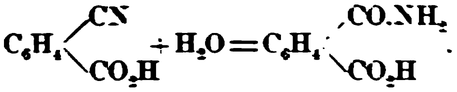
[2] *Ber. Deutsch. Chem. Ges.* x. 1742.

[3] Schreder, *ibid.* vii. 707.

Terephthalyl chloride, $C_6H_4(COCl)_2$, is formed by the distillation of the acid with phosphorus pentachloride and is a crystalline mass, which has a somewhat sharp odour resembling cinnamon, melts at 78° (Schreder) and boils at 259° (Beyer).

Terephthalamide, $C_6H_4(CO.NH_2)_2$, is obtained by the action of ammonia on the chloride, as a white amorphous powder, which is insoluble in all solvents (Warren de la Rue and Müller).

Terephthalamic acid, $C_6H_4(CO.NH_2)CO_2H$, is obtained as the product of all reactions by which paracyanobenzoic acid might be prepared, as the elements of water are taken up by the latter according to the following equation:



$$C_6H_4\begin{cases}CN\\CO_2H\end{cases} + H_2O = C_6H_4\begin{cases}CO.NH_2\\CO_2H\end{cases}.$$

Terephthalamic acid crystallizes in indistinct, microscopic plates, which are slightly soluble in cold, readily in hot water and alcohol, melt at 214°, and are converted into terephthalic acid by boiling with caustic soda (Sandmeyer).

Ethyl paracyanobenzoate, $C_6H_4(CN)CO_2C_2H_5$, is prepared from ethyl paramidobenzoate and crystallizes in needles, melting at 54°. On heating with an alcoholic solution of hydroxylamine, the ethyl ether of *benzenylamidoximeparacarboxylic acid*, $C_6H_4(CO_2H)C(NH_2)NOH$, is formed; it melts at 135° and yields the free acid which melts above 330°.[1] The meta- and para-cyanobenzoic acids and their ethers, therefore, behave towards hydroxylamine like other nitrils, while the ortho-compounds differ from these.

Terephthalonitril, $C_6H_4(CN)_2$, is prepared by heating terephthalamide with phosphorus pentoxide (Warren de la Rue and Müller) or by distilling potassium benzeneparadisulphonate,[2] potassium parachlorobenzenesulphonate,[3] or potassium parabromobenzenesulphonate [4] with potassium cyanide or dehydrated potassium ferrocyanide.[5] It is insoluble in water, slightly soluble in cold, readily in hot alcohol, and crystallizes in needles or lustrous prisms, which melt at 215° and readily sublime. It is converted into terephthalic acid by boiling with an aqueous, or more rapidly with an alcoholic, solution of potash. It is, however, better to decompose it by heating to 160° with hydrochloric acid (Limpricht).

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[1] Müller, *Ber. Deutsch. Chem. Ges.* xviii. 2485; xix. 1491.

[2] Garrick, *Zeitschr. Chem.* 1869, 551.

[3] Nölting, *Ber. Deutsch. Chem. Ges.* viii. 1110.

[4] Irelan, *Zeitschr. Chem.* 1869, 164; Barth and Senhofer, *Ann. Chem. Pharm.* 174, 242.

[5] Limpricht, *ibid.* clxxx. 88.

ADDITION PRODUCTS OF TEREPHTHALIC ACID.[1]

2253 *Tetrahydroterephthalic acid*, $C_6H_8(CO_2H)_2$. In order to prepare this substance, 5 grms. of terephthalic acid are dissolved in a little caustic soda solution and boiled for twenty hours, 500 grms. of 4 per cent. sodium amalgam being gradually added.

It is scarcely soluble in cold water and requires 120 parts of boiling water for solution, from which it crystallizes on cooling in small, arborescent prisms, which melt above 300° and sublime. Its silver salt is a white amorphous precipitate which blackens in the light.

Methyl tetrahydroterephthalate, $C_6H_8(CO_2.CH_3)_2$, is formed by the action of methyl iodide on the silver salt, as well as by passing hydrochloric acid into a solution of the acid in wood-spirit. It is thus obtained as an oily liquid, which smells of fennel and soon solidifies in large prisms, melting at 39°. It crystallizes from ether, in which it forms a blue fluorescent solution, in long needles.

Hexhydroterephthalic acid, $C_6H_{10}(CO_2H)_2$, is obtained by heating the tetrahydro-acid to 240° for six hours with concentrated hydriodic acid. It is even less soluble in water than the tetrahydro-compound and crystallizes from hot water in small prisms, melting at about 295°. It is very stable towards alkaline permanganate solution, while the tetrahydro-derivative is oxidized to oxalic acid by this even in the cold. Its methyl ether melts at 58° and resembles the preceding compound, but does not give a fluorescent solution.

Dibromohexhydroterephthalic acid, $C_6H_8Br_2(CO_2H)_2 + H_2O$, is best prepared by treating finely divided tetrahydroterephthalic acid for several hours with an ethereal solution of bromine, the mixture being agitated at intervals, and repeating this operation until the acid is almost completely dissolved. The solution is then decolourized with sulphur dioxide and the acid extracted by carbonate of soda solution. It is precipitated from the latter by hydrochloric acid in granular, cubic crystals. Its methyl ether is formed by the combination of bromine with the ether of tetrahydroterephthalic acid, and crystallizes in large prisms melting at 73°.

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[1] Baeyer, *Ber. Deutsch. Chem. Ges.* xix. 1805.

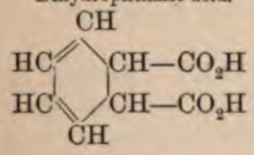
Tetrahydrophthalic acid behaves towards bromine in the same manner as cinnamic and fumaric acids. When the brominated acid is heated with caustic soda solution, a dihydroterephthalic acid is formed, which resembles terephthalic acid very closely. A syrupy acid is however formed by the action of freshly precipitated silver oxide, which is probably a dihydroxyhexhydroterephthalic acid, and is converted by the action of bromine into tetrabromocatechol:

$$C_6H_8(OH)_2(CO_2H)_2 + 7Br_2 = C_6Br_4(OH)_2 + 2CO_2 + 10HBr.$$

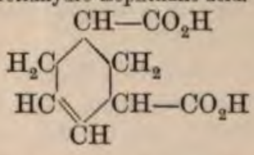
The constitution of tetrahydrophthalic acid is proved by the formation of this substance, and may also be deduced from the following considerations.

Phthalic acid only assumes two atoms of hydrogen when acted upon by sodium amalgam and water, while isophthalic and terephthalic acids combine with four. The simplest explanation of this fact is that the double linking of two carbon atoms is converted into a single one, if at least one of these be combined with a carboxyl group. The following formulæ are thus arrived at:

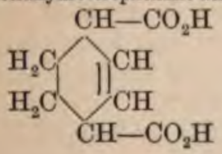
Dihydrophthalic acid.



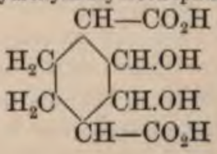
Tetrahydro-isophthalic acid.



Tetrahydroterephthalic acid.



Dihydroxyhexhydroterephthalic acid.



SUBSTITUTION PRODUCTS OF TEREPHTHALIC ACID.

2254 *Chloroterephthalic acid*, $C_6H_3Cl(CO_2H)$, is prepared from amidoterephthalic acid, and is slightly soluble in hot water, more readily in alcohol. It is crystalline, and melts above 300°. The chloride, $C_6H_3Cl(COCl)_2$, obtained by the action of phosphorus chloride, is also crystalline and boils at about 300°. By treating this with ammonium carbonate, the amide, $C_6H_3Cl(CO.NH_2)_2$, is formed, and crystallizes from alcohol in crusts, melting above 300°.

Methyl chloroterephthalate, $C_6H_3Cl(CO_2.CH_3)_2$, forms silky plates, melting at 60.°[1]

Bromoterephthalic acid, $C_6H_3Br(CO_2H)_2 + H_2O$, is formed by the action of potassium permanganate on an alkaline solution of bromoparatoluic acid. It is almost insoluble in cold water, and crystallizes from hot water in dazzling white, microscopic needles, which melt at 304°—305°. Phosphorus pentachloride converts it into the chloride, $C_6H_3Br(COCl)_2$, an oily liquid, which boils at 304·5°—305·5°, is only gradually decomposed by water, and combines with aqueous ammonia to form the amide, $C_6H_3Br(CO.NH_2)_2$, which crystallizes from hot water in small needles, melting at 270°.

Methyl bromoterephthalate, $C_6H_3Br(CO_2.CH_3)_2$, crystallizes in concentrically arranged groups of needles, melts at 42° and boils at above 300°.[2]

Dibromoterephthalic acid, $C_6H_2Br_2(CO_2H)_2$, is prepared by heating dibromocymene, $C_6H_2Br_2(CH_3)C_3H_7$, for some time with nitric acid,[3] and by the oxidation of dibromotoluic acid with potassium permanganate.[4] It crystallizes from hot, dilute alcohol in small plates, which have a satin lustre, do not melt even at 320°, and sublime at a higher temperature with decomposition.

Ethyl dibromoterephthalate crystallizes from alcohol in nacreous plates, melts at 121° and boils at about 335°.

Nitroterephthalic acid, $C_6H_3(NO_2)(CO_2H)_2$, is formed by treating terephthalic acid with a mixture of fuming sulphuric and nitric acids, and crystallizes in prisms; it separates from hot water in cauliflower-like masses, which melt at [illegible]

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[1] Ahrens, *Ber. Deutsch. Chem. Ges.* xix. 1634.
[2] Fischli, *ibid.* xii. 619.
[3] Claus and Wimmel, *ibid.* xiii. 902.
[4] Schultz, *ibid.* xviii. 1762.

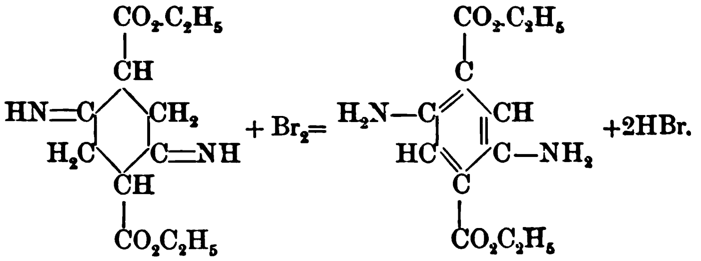
Methyl nitroterephthalate, $C_6H_3(NO_2)(CO_2CH_3)_2$, crystallizes from ether in splendid prisms, which melt at [illegible]

Nitroterephthalamide, $C_6H_3(NO_2)(CO.NH_2)_2$, was obtained by Warren de la Rue and Müller in well formed prisms by the nitration of terephthalamide.

Amidoterephthalic acid, $C_6H_3(NH_2)(CO_2H)_2$, is formed by the reduction of the nitro-acid with tin and hydrochloric acid, and crystallizes in thin, lemon-yellow prisms or moss-like forms, which are only slightly soluble in cold water and alcohol, and decompose on heating without melting. Their aqueous or alkaline solutions, and those of their salts and ethers, which latter are crystalline bodies but have not been described in detail, show a remarkable blue fluorescence, while acidified solutions of the acid do not possess this property.

Methyl amidoterephthalate, $C_6H_3(NH_2)(CO_2CH_3)_2$, forms crystals, melting at 126°; its alcoholic and ethereal solutions also show a strong blue fluorescence (Ahrens).

Diamidoterephthalic acid, $C_6H_2(NH_2)_2(CO_2H)_2$, is not known in the free state; its ethyl ether has been prepared from succinosuccinic ether (Pt. III., p. 146). When the latter is heated with ammonium acetate, a di-imide is formed, which crystallizes in shining, yellow needles, melting at 181°. *Diethyl-diamidoterephthalate* is obtained by the action of bromine on its solution in sulphuric acid:



It crystallizes from hot alcohol in lustrous golden needles of the colour of potassium dichromate, which melt at 168°. Its brown alcoholic or ethereal solution shows a golden-yellow fluorescence. It forms slightly soluble salts with hydrochloric and sulphuric acids.

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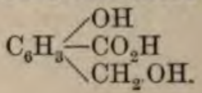
[1] Warren de la Rue and Müller, *Ann. Chem. Pharm.* cxxi. 90; Burckhardt, *Ber. Deutsch. Chem. Ges.* x. 144.

[2] Ahrens, *ibid.* xix. 1634.

When a solution of its diazo-compound in hydrochloric acid is heated with an acid solution of cuprous chloride, an acid is formed which is probably dichloroterephthalic acid, since it is converted into terephthalic acid by the action of sodium amalgam and water.[1]

Sulphoterephthalic acid, $C_6H_3(SO_3H)(CO_2H)_2$, is obtained by heating terephthalic acid with fuming sulphuric acid,[2] and by the oxidation of sulphoparatoluic acid, paratoluylsulphamic acid, or paraxylenesulphonic acid with potassium permanganate.[3] It forms a hygroscopic mass, and yields salts which are soluble in water, but insoluble in alcohol.

HYDROXYMETHYLHYDROXYBENZOIC ACID,



$$C_6H_3\begin{cases}OH\\CO_2H\\CH_2.OH.\end{cases}$$

2255 These compounds, which are simultaneously alcohols and phenols, are formed by the action of sodium amalgam on the aldehydo-acids, which are described below.[4]

Orthohydroxymethylsalicylic acid (1 : 2 : 6) is precipitated by acids from its alkaline solution as an oil, which solidifies after some time to hard, white crystals; it is readily soluble in hot water, alcohol and ether, and crystallizes from the latter in transparent prisms, which melt at 142°. Its aqueous solution is coloured an intense bluish-violet by ferric chloride.

Parahydroxymethylsalicylic acid (1 : 2 : 4) is slightly soluble in alcohol and ether, and crystallizes from the latter in long prisms, which melt at 160° with decomposition. Ferric chloride colours the solution violet.

Orthohydroxymethylparahydroxybenzoic acid (1 : 4 : 2) is a white powder, which does not melt below 270°, and gives no colouration with ferric chloride.

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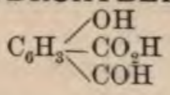
[1] Baeyer, *Ber. Deutsch. Chem. Ges.* xix. 428.

[2] Ascher, *Ann. Chem. Pharm.* clxi. 2 ; Schoop, *Ber. Deutsch. Chem. Ges.* xiv. 223.

[3] Hall and Remsen, *ibid.* xii. 1434 ; Burney and Remsen, *Amer. Chem. Journ.* ii. 405 and 413.

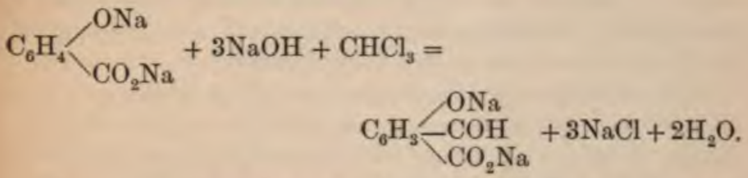
[4] Reimer, *Ber. Deutsch. Chem. Ges.* xi. 790.

ALDEHYDOHYDROXYBENZOIC ACIDS,



$$C_6H_3\begin{cases}OH\\CO_2H\\COH\end{cases}$$

2256 These are prepared by heating the hydroxybenzoic acids with caustic soda and chloroform:



$$C_6H_4\begin{cases}ONa\\CO_2Na\end{cases} + 3NaOH + CHCl_3 = C_6H_3\begin{cases}ONa\\COH\\CO_2Na\end{cases} + 3NaCl + 2H_2O.$$

They are converted by reduction into the preceding alcohol-acids, and by fusion with caustic potash into the hydroxyphthalic acids. They combine, like other aldehydes, with the sulphites of the alkali metals.

Ortho-aldehydosalicylic acid (1 : 2 : 6) is obtained, together with the following compound, from salicylic acid. It crystallizes in fine, matted needles, which dissolve at 23°—25° in 1,500—1,600 parts, or at 100° in 15—16 parts of water. The aqueous solution is coloured deep yellow by caustic soda, and red by ferric chloride, and the alcoholic solution shows a faint, bluish violet fluorescence. It melts at 179° and sublimes without decomposition when carefully heated. On distillation with slaked lime it decomposes into salicylaldehyde and carbon dioxide. The copper salt is a gelatinous precipitate, which is soluble in ammonia; on boiling the solution a light blue precipitate of $C_8H_4O_4Cu$ is thrown down.

Para-aldehydosalicylic acid (1 : 2 : 4) forms long, fine needles, which melt at 248°—249°, and dissolve in 2,600—2,700 parts of water at 25°, and in 145—150 parts at 100°. Its aqueous solution is not coloured by caustic soda, while ferric chloride produces a deep cherry-red colouration. On distillation with lime, parahydroxybenzaldehyde is formed; its copper salt is also soluble in ammonia, but is not precipitated on boiling.[1]

Ortho-aldehydoparahydroxybenzoic acid (1 : 4 : 2), was obtained by Reimer and Tiemann from parahydroxybenzoic acid; it crystallizes from hot water in thin, arborescent prisms, which melt at 243°—244°, and sublime in splendid, white needles. Its aqueous solution is coloured deep yellow by caustic soda and brownish red by ferric chloride. Salicylaldehyde is formed when it is distilled with caustic lime.

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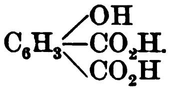
[1] Reimer and Tiemann, *Ber. Deutsch. Chem. Ges.* ix. 1268, x. 1562.

Ortho-aldehydometahydroxybenzoic acid (1 : 3 : 6) is obtained, together with the following compound, from metahydroxybenzoic acid. It crystallizes in needles, which melt at 234°, and are slightly soluble in hot water and readily in alcohol. Its aqueous solution is coloured violet by ferric chloride and deep yellow by caustic soda. On boiling with caustic soda it is only decomposed at a high temperature, phenol being formed.

Para-aldehydometahydroxybenzoic acid (1 : 3 : 4) has only been obtained as a syrup; it is very unstable and reduces Fehling's solution readily. On fusion with caustic potash it is converted into a-hydroxyisophthalic acid.[1]

HYDROXYPHTHALIC ACIDS,



$$C_6H_3\begin{cases}OH\\CO_2H\\CO_2H\end{cases}$$

2257 *a-Hydroxyphthalic acid* (4 : 1 : 2). When the ethyl ether of a-amidophthalic acid is dissolved in dilute sulphuric acid, treated with sodium nitrite and then heated to 100°, the ether of a-hydroxyphthalic acid separates out as a yellowish oil, which yields the free acid on saponifying with potash; it is purified by precipitating the neutral solution with basic lead acetate and removing the lead by sulphuretted hydrogen.[2] It is also obtained by oxidizing the sulphamido-orthotoluic acids with potassium permanganate and fusing the residue with potash,[3] and is formed when para-aldehydometahydroxybenzoic acid,[4] a-chlorophthalic acid,[5] and a-sulphophthalic acid [6] are fused with caustic potash or soda.

It is tolerably soluble in cold, very readily in hot water and alcohol, and crystallizes in large stellate groups of pointed prisms which melt at about 185°, the anhydride being formed; on heating with dilute hydrochloric acid to 180°, it decomposes into carbon dioxide and metahydroxybenzoic acid (Rée). Its aqueous solution is coloured reddish yellow by ferric chloride. When the acid is heated with resorcinol, hydroxyfluoresceïn is obtained, which forms a dark, yellowish red solution in caustic potash, and is slightly soluble in water with a yellowish green fluorescence; acids separate it from its alkaline solution as a yellow precipitate.

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[1] Landshoff and Tiemann, *Ber. Deutsch. Chem. Ges.* xii. 1334.

[2] Baeyer, *ibid.* x. 1079.

[3] Jacobsen, *ibid.* xiv. 42.

[4] Tiemann and Landshoff, *ibid.* xii. 1337.

[5] Krüger, *ibid.* xviii. 1759.

[6] Gräbe, *ibid.* xviii. 1130 ; Rée, *Inaugurald. Bern.* 1886.

a-Hydroxyphthalic anhydride, $C_8H_4O_4$, sublimes in feathery needles, when the acid is heated and melts at 165°—166°.

a-Methylhydroxyphthalic acid, $C_6H_3(OCH_3)(CO_2H)_2$, is formed by the oxidation of methylparahydroxyorthotoluic acid with potassium permanganate, and crystallizes from water in stellate groups of needles, which lose water on heating, forming the anhydride, which sublimes in long needles and melts at 93°.[1]

v-Hydroxyorthophthalic acid (3 : 1 : 2) is prepared by gently fusing v-methylhydroxyphthalic acid with potash, and by means of the diazo-reaction from the product of reduction of a-nitrophthalic acid, which contains amidophthalic acid. It separates from hot water as a compact, crystalline mass, consisting of short, hard prisms, which are partly converted by heating into the anhydride, melting at 145°—148°, and are partly decomposed into phenol and carbon dioxide. Its aqueous solution is coloured a deep cherry-red by ferric chloride. When it is heated to 200° with resorcinol, hydroxyfluoresceïn is formed.

Dinitro-v-hydroxyphthalic acid, $C_6H(NO_2)_2(OH)(CO_2H)_2$, was first obtained by the action of nitric acid on juglon, a hydroxynaphthoquinone, $C_{10}H_5(OH)O_2$, which occurs in green walnut shells (*Juglans regia*), and was called *juglonic acid*. It may also be prepared by the nitration of v-hydroxyphthalic acid; it is exceptionally soluble in water, alcohol and ether, and separates from petroleum ether in small crystals. Its acid potassium salt, $C_8H_3KN_2O_9$, crystallizes in yellow, rhombic plates, which detonate violently on heating. It can be recrystallized from nitric acid or dilute sulphuric acid without undergoing decomposition.[2]

v-Methylhydroxyphthalic acid has been prepared by the oxidation of v-methylorthohomometahydroxybenzoic acid; it is tolerably soluble in water, and crystallizes in microscopic prisms, which melt at 160°, and are thus converted into the anhydride, which sublimes in needles and melts at 87°.[3]

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[1] Schall, *Ber. Deutsch. Chem. Ges.* xii. 829.

[2] Bernthsen and Semper, *ibid.* xviii. 210; xix. 164.

[3] Jacobsen, *ibid.* xvi. 1962.

2258 *a-Hydroxyisophthalic acid* (4 : 1 : 3) is formed, together with a large quantity of hydroxytrimesic acid, $C_6H_2(OH)(CO_2H)_3$, when carbon dioxide is passed over disodium salicylate heated to 370°—380°.[1] It may be obtained in a similar manner from parahydroxybenzoic acid, which first changes into salicylic acid.[2] It is also formed by the oxidation of para-aldehydosalicylic acid or ortho-aldehydoparahydroxybenzoic acid with potassium permanganate, and when this acid,[3] a-metaxylenol,[4] or a-metaxylenesulphonic acid,[5] is fused with potash. When an alkaline solution of salicylic acid is heated to 120°—130° with tetrachloromethane, a-hydroxyisophthalic acid is obtained, together with a little v-hydroxyisophthalic acid.[6]

In order to prepare it, phenol is dissolved in an alkaline solution which contains one molecule of potash to three of soda, the mass evaporated and carbon dioxide passed over the dry residue for some time at 120°—160°, the temperature being finally raised to 300°—320°. The chief product of the reaction is a-hydroxyisophthalic acid accompanied by parahydroxybenzoic acid and hydroxytrimesic acid, almost two-thirds of the phenol coming over unchanged. The residue is decomposed with hydrochloric acid, and the a-hydroxyisophthalic acid repeatedly recrystallized from water.[7]

It forms long needles, which cross each other at an angle of 60°, melt at 305°—306°, and dissolve at 10° in 5,000, at 24° in 3,000, and at 100° in 160 parts of water. It is readily soluble in alcohol and ether, but not in chloroform, by means of which it can be separated from hydroxytrimesic acid. Its aqueous solution is coloured a deep cherry-red by ferric chloride. On heating to 200° with hydrochloric acid, it decomposes into phenol and carbon dioxide, while on dry distillation it yields salicylic acid, phenol and carbon dioxide. When its disodium salt, $C_6H_3(OH)(CO_2Na)_2$, is heated to 250°, the trisodium salt, $C_6H_3(ONa)(CO_2Na)_2$, is obtained, together with phenol and carbon dioxide, while the potassium salt yields a large amount of parahydroxybenzoic acid when heated to 280°—300° (Ost).

a-Methoxyisophthalic acid, $C_6H_3(OCH_3)(CO_2H)_2$, is formed by the oxidation of a-metaxylenyl monomethyl ether,[1] or methylparahomosalicylic acid[2] with potassium permanganate, and crystallizes from hot water in microscopic needles, melting at 261° (Schall).

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[1] Ost, *Journ. Prakt. Chem.* [2] xiv. 99.
[2] Kupferberg, *ibid.* [2] xvi. 428.
[3] Tiemann and Reimer, *Ber. Deutsch. Chem. Ges.* x. 1571.
[4] Jacobsen, *ibid.* xi. 377.
[5] Jacobsen and Remsen, *ibid.* xi. 377.
[6] Hasse, *ibid.* x. 2195.
[7] Ost, *Journ. Prakt. Chem* [2] xv. 301

Dimethyl a-hydroxyisophthalate, $C_6H_3(OH)(CO_2.CH_3)_2$, forms large, flat needles which melt at 96° (Jacobsen).

Diethyl a-hydroxyisophthalate, $C_6H_3(OH)(CO_2.C_2H_5)_2$, crystallizes in fine needles, which melt at 52° and are soluble in caustic soda (Ost).

v-Hydroxyisophthalic acid (2:1:3) is formed when orthoaldehydosalicylic acid[3] or sulphamido-isophthalic acid[4] is fused with potash. It crystallizes in hair-like needles, which melt at 243°—244°, dissolve in 700 parts of water at 24°, and in 35-40 parts at 100°. Ferric chloride produces a cherry-red colouration; the aqueous and alcoholic solutions show a bluish violet fluorescence, which is destroyed by alkalis. The acid decomposes on heating, the chief portion being resolved into salicylic acid and carbon dioxide.

v-Methoxyisophthalic acid, $C_6H_3(OCH_3)(CO_2H)_2$, is prepared by the oxidation of methylorthohomosalicylic acid and crystallizes from water in prisms, which melt at 216°—218°, turning brown and subliming at the same time (Schall).

s-Hydroxyisophthalic acid (5:1:3) is obtained by fusing s-sulpho-isophthalic acid with potash, and by means of the diazo-reaction from amido-isophthalic acid. It crystallizes from hot water, in which it readily dissolves, in fascicular groups of needles with two molecules of water, which are lost at 100°. It melts at 288° and sublimes in broad, lustrous needles, which dissolve in 3280 parts of water at 5° and are coloured a faint yellow by ferric chloride. It decomposes into phenol and carbon dioxide on distillation with lime:[5]

	Melting-point.
Dimethyl s-hydroxyisophthalate, $C_6H_3(OH)(CO_2.CH_3)_2$, fine needles	160°
Diethyl s-hydroxyisophthalate, $C_6H_3(OH)(CO_2.C_2H_5)_2$ monoclinic prisms	103°

2259 *Hydroxyterephthalic acid* (2:1:4) was prepared by Warren de la Rue and Müller from amidoterephthalic acid by the action of nitrous acid.[1] It is also formed when paraxylenol,[2] bromoterephthalic acid,[3] ortho-aldehydometahydroxybenzoic acid,[4] or metahydroxyparatoluic acid[5] is fused with caustic potash.

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[1] Jacobsen, *Ber. Deutsch. Chem. Ges.* xi. 898.

[2] Schall, *ibid.* xii. 828.

[3] Tiemann and Riemer, *ibid.* x. 1570.

[4] Jacobsen.

[5] Heine, *Ber. Deutsch. Chem. Ges.* xii. 494; Lönnies, *ibid.* xiii. 705.

In order to prepare it, amidoterephthalic acid is dissolved in dilute sulphuric acid, treated with sodium nitrite and boiled.[6] It forms a powder, which is slightly soluble in hot water, readily in alcohol, and sublimes on heating with partial decomposition without previously melting. Its aqueous solution is coloured an intense violet-red by ferric chloride. When it is mixed with sand and submitted to dry distillation, it decomposes into carbon dioxide and phenol, and on heating with hydrochloric acid to 220° is resolved into carbon dioxide and metahydroxybenzoic acid, while fusion with an excess of caustic potash converts it into salicylic acid, together with a smaller amount of metahydroxybenzoic acid.[7]

Methoxyterephthalic acid, $C_6H_3(OCH_3)(CO_2H)_2$, is formed by the oxidation of methylmetahomosalicylic acid[8] and crystallizes from hot water in small prisms, which melt at 277°—279°, and are resolved into methyl chloride and hydroxyterephthalic acid by hydrochloric acid at 160°.

Dimethyl hydroxyterephthalate, $C_6H_4(OH)(CO_2.CH_3)_2$, is obtained by passing hydrochloric acid into a solution of the acid in methyl alcohol, and crystallizes in splendid, silky needles, which melt at 94° and are soluble in hot water, readily in alcohol. Ferric chloride gives a somewhat fainter colouration than with the free acid. When the ethereal solution is shaken up with caustic soda solution, the sodium compound, $C_6H_3(ONa)(CO_2.CH_3)_2$, is formed as a white paste. On heating the acid with caustic soda, methyl iodide and wood-spirit, the trimethyl ether, $C_6H_3(OCH_3)(CO_2.CH_3)_2$, is obtained as an oily, pleasant-smelling liquid.

Dimethyl acetoxyterephthlate, $C_6H_3(OCO.CH_3)(CO_2.CH_3)_2$, is prepared by heating the dimethyl ether with acetyl chloride, and crystallizes from alcohol in cauliflower-like masses of fine needles, melting at 76° (Burckhardt).

Dinitrohydroxyterephthalic acid, $C_6H(NO_2)(OH)(CO_2H)_2$, is formed by the action of a mixture of concentrated nitric acid and fuming sulphuric acid on hydroxyterephthalic acid. It is readily soluble in water, from which it separates in golden yellow, transparent crystals, resembling those of calc-spar, which are, like the yellow and red salts of the acid, explosive.[1]

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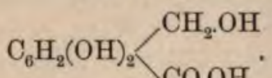
[1] *Ann. Chem. Pharm.* cxxi. 96.
[2] Jacobsen, *Ber. Deutsch. Chem. Ges.* xi. 570.
[3] Fischli, *ibid.* xii. 621.
[4] Tiemann and Landshoff, *ibid.* xii. 1336.
[5] Hall and Remsen, *ibid.* xii. 1433.
[6] Burckhardt, x. 144.
[7] Barth and Schreder, xii. 1260.
[8] Schall, *ibid.* xii. 828.

HYDROXYMETHYLDIHYDROXYBENZOIC ACIDS,



$$C_6H_2(OH)_2\begin{cases}CH_2.OH\\CO.OH\end{cases}.$$

2260 In 1832, Couerbe detected *meconin*,[2] $C_{10}H_{10}O_4$, in opium, and Wöhler and Liebig, in 1842, obtained *opianic acid*,[3] $C_{10}H_{10}O_5$, by the oxidation of narcotin or opian, which is also an opium alkaloid. This acid was more closely investigated by Wöhler, who found that it is converted by further oxidation into *hemipinic acid*, $C_5H_5O_3$. He assumed that in its formation one molecule of opianic acid took up oxygen and formed two molecules of hemipinic acid; he says: "It contains a radical which consists of half the radical of opianic acid, and this is referred to in its name." [4]

Anderson, who also investigated the products of oxidation of narcotin, obtained a substance, *opianyl*, in addition to these acids, and pointed out that it shows an interesting relation to opianic and hemipinic acids when the formula of the latter of these is doubled, as his and Laurent's[5] researches had shown to be necessary. "For we have as follows:

Opianyl	$C_{10}H_{10}O_4$,
Opianic acid . . .	$C_{10}H_{10}O_5$,
Hemipinic acid .	$C_{10}H_{10}O_6$,

as though these three compounds were different oxidation products of the same radical." [6]

He subsequently found that opianyl is identical with meconin.[7]

Matthiessen and Foster then made the important observation, that when opianic acid is evaporated with caustic potash solution it is resolved into meconin and hemipinic acid:

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[1] Burckhardt, *Ber. Deutsch. Chem. Ges.* xii. 1273.

[2] *Ann. Chim. Phys.* xlix. 44; l. 337; lix. 148.

[3] *Ann. Chem. Pharm.* xliv. 126.

[4] *Ibid.* l. 1.

[5] *Compt. Rend.* xx. 1118.

[6] *Ibid.* lxxxvi. 179.

[7] *Ibid.* xcviii. 44.

$$2C_{10}H_{10}O_5 = C_{10}H_{10}O_4 + C_{10}H_{10}O_6.$$

They also found that opianic acid is reduced to meconin by the action of water and sodium amalgam:

$$C_{10}H_{10}O_5 + 2H = C_{10}H_{10}O_4 + H_2O.$$

These highly characteristic reactions receive, according to them, a simple explanation, if it be assumed that a very unstable hydrate of meconin, $C_{10}H_{12}O_5$, is first formed. The decomposition of opianic acid then becomes quite analogous to that of benzaldehyde into benzyl alcohol and benzoic acid, and the reduction of the former also corresponds to that of benzaldehyde to benzyl alcohol.

By heating hemipinic acid with concentrated hydriodic acid, they obtained carbon dioxide, methyl iodide and *hypogallic acid*, according to the equation:

$$C_{10}H_{10}O_6 + 2HI = CO_2 + 2CH_3I + C_7H_6O_4.$$

If hydrochloric acid be employed, *methylhypogallic acid*, $C_8H_8O_4$ is first formed, and is converted into hypogallic acid by further heating.

Hemipinic acid, therefore, as well as opianic acid and meconin, contains two methyl groups, and the three bodies in question are derivatives of the still unknown normal compounds:

Normeconin	$C_8H_6O_4$,
Noropianic acid . .	$C_8H_6O_5$,
Norhemipinic acid .	$C_8H_6O_6$,

as they may be shortly designated, ordinary meconin being thus dimethylnormeconin &c.

They then succeeded in converting the latter, as well as opianic acid, into *methylnormeconin*, $C_9H_8O_4$, and *methylnoropianic acid*, $C_9H_8O_5$, by heating with hydrochloric or hydriodic acid. They finally considered hemipinic acid to be dimethyldihydroxyterephthalic acid and looked upon opianic acid as the corresponding aldehydo-acid,[1] but, as shown by Matthiessen and Wright, the former can be readily converted into an anhydride, and must therefore be *dimethyldihydroxyphthalic acid*.

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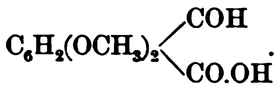
[1] *Phil. Trans.* 1863, 345; *Journ. Chem. Soc.* [2] i. 342; *ibid.* vi. 357.

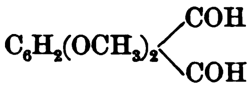
Liebermann and Chojnacki proposed the following formula for opianic acid:



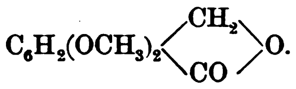
$$\mathrm{C_6H_2(OCH_3)_2}\left\langle\begin{matrix}\mathrm{COH}\\ \mathrm{CO.OH}\end{matrix}\right. .$$

and this was confirmed by the researches of Beckett and Wright, who also found that hypogallic acid is identical with protocatechuic acid.

In the case of meconin there were two possibilities; it might be either hemipinic aldehyde or the anhydride of an alcoholic acid:



$$\mathrm{C_6H_2(OCH_3)_2}\left\langle\begin{matrix}\mathrm{COH}\\ \mathrm{COH}\end{matrix}\right.$$



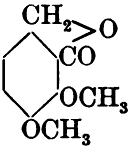
$$\mathrm{C_6H_2(OCH_3)_2}\left\langle\begin{matrix}\mathrm{CH_2}\\ \mathrm{CO}\end{matrix}\right\rangle\mathrm{O}.$$

The facts that it is formed from opianic acid by the action of nascent hydrogen, and cannot be re-oxidized to opianic acid, while the latter is converted into meconin and hemipinic acid by heating with caustic potash, are in favour of the latter view.

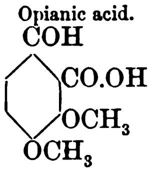
Beckett and Wright then proved that this view is correct, and their results were confirmed by the researches of Hessert.[1] Hemipinic acid is dimethylcatecholdicarboxylic acid, and can readily be converted into protocatechuic acid or catecholcarboxylic acid, in which the side-chains have the position $CO_2H : OH : OH = 1 : 3 : 4$. Since hemipinic acid is simultaneously a derivative of phthalic acid, the second carboxyl group must be either in position 2 or 6; in the latter case it would yield only one acid methyl ether, while in the former two such compounds would be possible. Wegscheider has now found that two such isomerides exist,[2] and he has also obtained isovanillin by heating opianic acid with dilute hydrochloric acid,[3] while Beckett and Wright found that methylvanillin is formed when sodium opianate is distilled with soda-lime.

It follows from these facts that the constitutions of the three compounds in question are represented by the following formulæ:

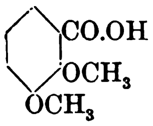
Meconin.



Opianic acid.



Hemipinic acid.



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[1] *Journ. Chem. Soc.* 1876, i. 164, 281, 461.

[2] *Monatsh. Chem.* iii. 348.

[3] Ibid. iii. 708.

Meconin therefore stands to hemipinic acid in the same relation as phthalide to phthalic acid.

2261 *Meconinic acid* or *Hydroxymethyldimethoxybenzoic acid*, $C_6H_2(OCH_3)_2(CH_2.OH)CO_2H$, is not known in the free state. When its lactone, meconin, is dissolved in baryta water, *barium meconinate*, $(C_{10}H_{11}O_5)_2Ba$, is formed, and is left on evaporation as a gummy mass[1] (Kessert), while Prinz obtained it in fine, silky needles.[2] This salt, however, yields meconin on decomposition with a strong acid. The copper and silver salts are precipitates, which decompose on heating with formation of meconin.

Meconin, $C_{10}H_{10}O_4$, as already mentioned, occurs in opium. Anderson obtained it, accompanied by other products, by the oxidation of narcotin with nitric acid, and it is also formed by the reduction of opianic acid.

In order to prepare it, the mother liquor of the opium alkaloids is extracted with ether, the solution evaporated, and the residue washed with hydrochloric acid and re-crystallized from water (Anderson). It forms white, lustrous needles, which have a bitter taste, melt at 102°—102°·5 (Wright), and when carefully heated sublime in splendid needles. It is readily soluble in alcohol and ether, and requires 22 parts of boiling water and 700 parts of water at 15·5° for solution. On heating with concentrated sulphuric acid, a purple-coloured solution is formed.

It forms ethers when heated with stearic or benzoic acids, as was shown by Berthelot, who concluded from this that it is an alcohol.[3]

Chloromeconin, $C_{10}H_9ClO_4$, was prepared by Anderson by the action of chlorine on fused meconin or on its aqueous solution. It crystallizes in colourless needles, which are scarcely soluble in cold, somewhat more readily in hot water, and more freely in alcohol, melt at 175° and sublime without decomposition.

Bromomeconin, $C_{10}H_9BrO_4$, crystallizes from alcohol in colourless needles, melting at 167°.

Iodomeconin, $C_{10}H_9IO_4$, is formed by the action of chloride of iodine on an aqueous solution of meconin, and forms long crystals or needles, which melt at 112°, and decompose when more strongly heated.

Nitromeconin, $C_{10}H_9(NO_2)_2O_4$, is obtained by dissolving meconin in cold, concentrated nitric acid, and precipitating with water. It crystallizes from alcohol in white needles or prisms, which melt at 160°, and sublime when carefully heated. It forms a yellow solution in hot alkalis and is not re-precipitated by acids, nitromeconinic acid being probably formed.

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[1] *Ber. Deutsch. Chem. Ges.* xi. 240.

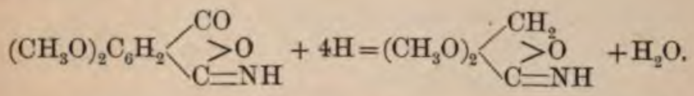
[2] *Journ. Prakt. Chem.* [2] xxiv. 373.

[3] *Ann. Chim. Phys.* [3] lvi. 51 ; *Ann. Chem. Pharm.* cxii. 356.

Amidomeconin, $C_{10}H_9(NH_2)O_4$, is prepared by warming the preceding compound with iron filings and acetic acid. It is precipitated by water as a yellowish powder, which is only slightly soluble in benzene, and melts at 171°.

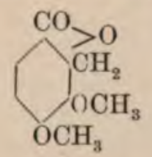
Methyl normeconin, $C_6H_2(OCH_3)(OH)C_2H_2O_2$, is formed when meconin is heated with hydrochloric or hydriodic acid (Matthiessen and Foster), and when meconin or narcotin is carefully fused with caustic potash (Beckett and Wright). It crystallizes from hot water in prisms, which melt at 125°; ferric chloride colours the aqueous solution a beautiful blue, which is converted into red by the addition of ammonia. On further fusion with potash it is converted into protocatechuic acid.

ψ-Meconin. When hemipinimide, which will be further described below, is boiled with tin and hydrochloric acid, *hemipinimidine* is formed:



$$(CH_3O)_2C_6H_2\left<\begin{matrix}CO\\ >O\\ C{=}NH\end{matrix}\right. + 4H = (CH_3O)_2\left<\begin{matrix}CH_2\\ >O\\ C{=}NH\end{matrix}\right. + H_2O.$$

This substance crystallizes from benzene in small plates, which melt at 181°, and are converted into *nitrosohemipinimidine*, $C_{10}H_{10}O_3N(NO)$, by the action of sodium nitrite on their solution in hydrochloric acid. The latter compound crystallizes from hot alcohol in silky, yellow needles, and dissolves in caustic soda solution with evolution of nitrogen. Hydrochloric acid added to this solution precipitates ψ-meconin, which crystallizes from hot water in colourless needles, melting at 123°—124°. Its isomerism with meconin is shown by the following formula:



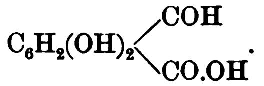
Nitro-ψ-meconin, $C_{10}H_9(NO_2)O_4$, crystallizes in splendid, yellowish needles, which melt at 166°.

Amido-ψ-meconin, $C_{10}H_9(NH_2)O_4$, resembles amidomeconin, but is readily soluble in benzene, and melts at 165°.[1]

[1] Salomon, *Ber. Deutsch. Chem. Ges.* xx. 883.

Meconiosin, $C_8H_{10}O_2$, also occurs in opium, and crystallizes in plates, which melt at 88° and dissolve in 27 parts of cold water, and in almost every proportion in boiling water. On heating with sulphuric acid a splendid green solution is formed.[1]

ALDEHYDODIHYDROXYBENZOIC ACIDS,



$$C_6H_2(OH)_2\begin{cases}COH\\CO.OH\end{cases}.$$

2262 *Noropianic acid*, $2C_8H_6O_5 + 3H_2O$, was obtained by Wright, together with methyl iodide, by boiling opianic acid with four times its weight of 50 per cent. hydriodic acid. It is readily soluble in water and crystallizes in fine prisms, which become anhydrous at 100° and melt at 171°. Its solution is coloured greenish blue by ferric chloride, the addition of ammonia or carbonate of sodium changing the colour to brownish red. It reduces ammoniacal silver solution in the cold and forms a yellow or brown solution in alkalis. The lead salt is a canary-yellow precipitate.[2]

Methylnoropianic acid, $C_6H_2(OCH_3)OH(COH)CO_2H$, was prepared by Matthiessen and Foster from opianic acid by heating it with hydrochloric or hydriodic acid. In order to prepare it, hydrochloric acid is passed into a warm solution of 50 grms. of opianic acid in 600 cb. cms. of strong hydrochloric acid until no opianic acid separates after standing for about two days. The solution is then concentrated, the paste of crystals thus obtained dissolved in water, the solution neutralized exactly with ammonia and treated with barium chloride, which produces a brown precipitate. The addition of ammonia to the filtrate precipitates the barium salt of the acid, which is then washed and decomposed with sulphuric acid.[3]

It is readily soluble in water and crystallizes in nacreous plates, long prisms, or transparent vitreous columns, which contain different amounts of water, but all readily effloresce in the air. The anhydrous acid melts at 154°; its aqueous solution is coloured dark blue by ferric chloride, and on the addition of ammonia light red.

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[1] T. and H. Smith, *Pharm. Journ. Trans.* [3] viii. 981.

[2] *Journ. Chem. Soc.* 1877, ii. 545.

[3] Prinz, *Journ. Prakt. Chem.* [2] xxiv. 368.

As a phenol-acid it forms two series of salts.

Silver methylnoropianate, $C_9H_7O_5Ag$, is a gelatinous precipitate, which becomes crystalline on standing. It is soluble in hot water and separates in crystals when the solution is cooled.

Barium methylnoropianate, $C_9H_8O_5Ba + H_2O$, is also thrown down in the gelatinous state and changes into granular crystals on standing.

Chloromethylnoropianic acid, $C_6HCl(OCH_3)OH(COH)CO_2H$, is obtained by the action of potassium chlorate and hydrochloric acid on methylnoropianic acid, and crystallizes from hot water in large, lustrous needles, which melt at 206° (Prinz).

Nitromethylnoropianic acid, $C_6H(NO_2)(OCH_3)OH(COH)CO_2H + H_2O$, is formed when methylnoropianic acid is treated with dilute nitric acid (Matthiessen and Foster). It is also obtained by heating nitro-opianic acid for some time with hydrochloric acid. It crystallizes in radiating needles, which lose their water at 120° and melt at 203°.[1]

2263 *Dimethylnoropianic acid* or *Opianic acid*, $C_6H_2(OCH_3)_2(COH)CO_2H$, was prepared by Wöhler and Liebig from narcotin by boiling it with dilute sulphuric acid and manganese dioxide. Blyth found that it is also formed by heating with platinum chloride,[2] and Anderson obtained it by oxidizing narcotin with dilute nitric acid. In order to prepare it according to the method proposed by Matthiessen and Foster, 100 grms. of narcotin are heated with 1,500 grms. of water and 150 grms. of sulphuric acid until the mixture boils; 150 grms. of finely powdered pyrolusite, corresponding to 90 grms. of manganese dioxide, are then added somewhat rapidly and the hot solution filtered.

Opianic acid separates out on cooling and is purified by recrystallization. Wöhler, in order to obtain it perfectly colourless, dissolved it in sodium hypochlorite, heated to boiling, and then added an excess of the hypochlorite. The decolourization may also be effected, according to Prinz, by passing the gases evolved from nitric acid and arsenic trioxide through the hot solution; and it may also be obtained perfectly white by running potassium permanganate into the hot solution acidified with sulphuric acid until it becomes sherry-yellow.[3] The portion which is left in the mother-liquor from its preparation can be removed by ether, which does not dissolve the colouring matter (Wegscheider).

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[1] Elbel, *Ber. Deutsch. Chem. Ges.* xix. 2306.
[2] *Ann. Chem. Pharm.* l. 29.
[3] Prinz, *Journ. Prakt. Chem.* [2] xxiv. 353.

It is slightly soluble in cold, readily in hot water, alcohol and ether, and crystallizes in thin, narrow prisms or silky needles, which melt at 150° (Wegscheider) and decompose on further heating, giving off a vapour which smells like vanilla (Wöhler). It has a faint acid reaction and a slightly bitter taste. Sodium amalgam and water reduce it to meconin, while on evaporation with caustic potash it is converted into the latter and hemipinic acid (Matthiessen and Foster, Beckett and Wright). When its sodium salt is heated with soda lime methylvanillin is formed, and isovanillin when it is heated with dilute sulphuric acid to 160°—170°. Concentrated sulphuric acid converts it on heating into a red colouring matter, which Anderson mistook for alizarin, $C_{14}H_8O_4$, but which was shown by Liebermann and Chojnacki to be the closely allied substance rufiopin,[1] $C_{14}H_8O_6$.

The salts of opianic acid have been investigated by Wöhler and Wegscheider.[2]

Potassium opianate, $C_{10}H_9O_5K$, is readily soluble in water and crystallizes in several forms, which differ in the amount of water they contain. It crystallizes from ordinary alcohol in compact, white prisms containing two and a half molecules, or transparent, rhombic tablets with one molecule of water of crystallization.

Barium opianate, $(C_{10}H_9O_5)_2Ba+2H_2O$, forms a radiating mass of prisms, which are readily soluble in water and effloresce when kept in a warm place.

Lead opianate, $(C_{10}H_9O_5)_2Pb + 2H_2O$, is only slightly soluble, and forms very lustrous, transparent crystals, apparently of the same form as sphenite.

Silver opianate, $2C_{10}H_9O_5Ag + H_2O$, is described by Wöhler as forming short prisms, which readily become coloured yellow. Wegscheider found that when the acid is rapidly dissolved in presence of silver carbonate, complete saturation does not take place, and that reduction ensues on boiling. On precipitating the potassium salt with silver nitrate, he found that the greater portion of the silver salt was removed by washing, and therefore prepared it by mixing concentrated solutions of silver fluoride and potassium opianate. The tough, amorphous, yellowish precipitate changes on stirring into hemispherical or warty masses consisting of small prisms, which can be completely washed with a small quantity of water.

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[1] *Ann. Chem. Pharm.* clxii. 321.

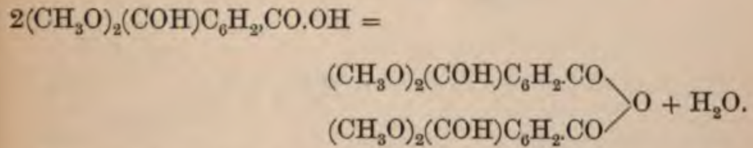
[2] *Monatsh. Chem.* iii. 348.

Methyl opianate, $C_{10}H_9O_5(CH_3)$, was prepared by Wegscheider from the silver salt by the action of methyl iodide. It is also formed, as found by Liebermann and Kleemann, when opianic acid is boiled with methyl alcohol.[1] It crystallizes from alcohol in flat, monosymmetric needles, and from ether in thick, vitreous tablets or short prisms, which melt at 102° and partially sublime on careful heating. It rapidly decomposes into methyl alcohol and opianic acid when boiled with water, the latter being obtained pure by this method (Liebermann and Kleemann).

Ethyl opianate, $C_{10}H_9O_5(C_2H_5)$, is readily formed, according to Wöhler, by saturating a hot, alcoholic solution of opianic acid with sulphur dioxide, while it could not be prepared by means of hydrochloric acid. Anderson, however, noticed its formation when hydrochloric acid was added to an alcoholic solution of the potassium salt, and Prinz prepared it by the action of the chloride on absolute alcohol. According to Liebermann and Kleemann, it may be most simply obtained by boiling the acid with absolute alcohol.

It crystallizes from alcohol in needles or fine prisms, which melt at 92° and sublime when carefully heated.

2264 *Opianic anhydride*, $C_{20}H_{18}O_9$. Wöhler found that opianic acid undergoes a remarkable change when it is kept in a state of fusion for some time, becoming insoluble in water, and he assumed that it is thus converted into an isomeric modification, while Matthiessen and Wright concluded that it loses water and forms the compound $C_{40}H_{38}O_{19}$.[2] Wegscheider, on the other hand, considered the substance to be formed from three molecules of opianic acid, and named it *triopianide*, $C_{30}H_{18}O_{14}$.[3]; Liebermann has, however, found[4] that it is formed when opianic acid is heated for two hours at 160° in a current of air, and explains the reaction by the following equation:



$$2(CH_3O)_2(COH)C_6H_2,CO.OH = \begin{matrix}(CH_3O)_2(COH)C_6H_2.CO\\(CH_3O)_2(COH)C_6H_2.CO\end{matrix}\!\!>O + H_2O.$$

Opianic anhydride is also obtained when opianic acid is heated with phosphorus pentachloride, and crystallizes from hot acetone in needles, which melt at 234°.

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[1] *Ber. Deutsch. Chem. Ges.* xx. 881.

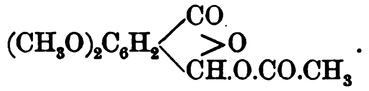
[2] *Ann. Chem. Pharm.* Suppl. vii. 63.

[3] *Monatsh. Chem.* iv. 262.

[4] *Ber. Deutsch. Chem. Ges.* xix. 2286.

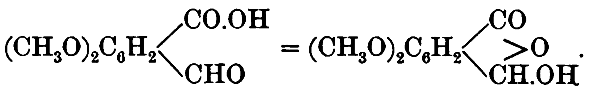
On heating with caustic potash and a little water, it decomposes into meconin and hemipinic acid, while on boiling with caustic potash solution, or when it is dissolved in sulphuric acid and the solution poured into water, it is reconverted into opianic acid.

Acetylopianic acid. When aromatic aldehydes or aldehydo-acids are heated with acetic anhydride and anhydrous sodium acetate, the aldehyde group CHO is converted into the acrylic acid residue $CH{=}CH{-}CO_2H$. Opianic acid does not behave in this way, but forms acetylopianic acid, which crystallizes from hot water in needles melting at 120°—121°. It is insoluble in cold alkalis and is only decomposed on boiling, acetic and opianic acids being formed; it therefore does not contain a carboxyl group, and its constitution must be expressed by the following formula:



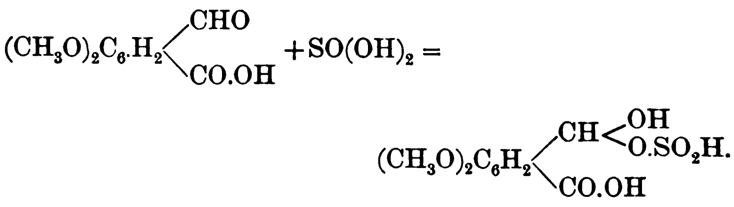
$$(\mathrm{CH_3O})_2\mathrm{C_6H_2}\left\langle\begin{matrix}\mathrm{CO}\\ >\mathrm{O}\\ \mathrm{CH.O.CO.CH_3}\end{matrix}\right. .$$

It appears, therefore, that opianic acid can behave not only as an ortho-aldehydo-acid, but also as a lactone.[1] The one form can pass into the other according to the circumstances of the case:



$$(\mathrm{CH_3O})_2\mathrm{C_6H_2}\left\langle\begin{matrix}\mathrm{CO.OH}\\ \mathrm{CHO}\end{matrix}\right. = (\mathrm{CH_3O})_2\mathrm{C_6H_2}\left\langle\begin{matrix}\mathrm{CO}\\ >\mathrm{O}\\ \mathrm{CH.OH}\end{matrix}\right. .$$

Opianyl sulphurous acid, $C_6H_2(OCH_3)_2(CHO.SO_3H_2)CO_2H$, is formed when opianic acid is dissolved in a hot aqueous solution of sulphur dioxide:



$$(\mathrm{CH_3O})_2\mathrm{C_6.H_2}\left\langle\begin{matrix}\mathrm{CHO}\\ \mathrm{CO.OH}\end{matrix}\right. + \mathrm{SO(OH)_2} =$$

$$(\mathrm{CH_3O})_2\mathrm{C_6H_2}\left\langle\begin{matrix}\mathrm{CH}\left\langle\begin{matrix}\mathrm{OH}\\ \mathrm{O.SO_2H}\end{matrix}\right.\\ \mathrm{CO.OH}\end{matrix}\right. .$$

On evaporation at a gentle heat, the compound is left as a fine crystalline mass, which is resolved into its constituents by water. Its solution has a characteristic bitter taste, and leaves a persistent, sweet after-taste.

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[1] Liebermann and Kleemann, *Ber. Deutsch. Chem. Ges.* xix. 2287.

Barium opianylsulphite, $(C_{10}H_{10}O_5.SO_3H)_2Ba+3H_2O$, is prepared by dissolving barium carbonate in a freshly-made solution of the acid, and crystallizes in lustrous, rhombohedral tablets.

Lead opianylsulphite, $(C_{10}H_{10}O_5.SO_2H)_2Pb+6H_2O$, is prepared in a similar manner, and forms very lustrous, four-sided prisms or six-sided tablets (Wöhler).

These salts correspond to the ethidene sulphites (Part II. p. 73).

2265 *Thio-opianic acid*, $(CH_3O)_2C_6H_2(CHS)CO_2H$, was obtained by Wöhler by passing sulphuretted hydrogen into a warm solution of opianic acid; it forms a yellow powder which crystallizes from alcohol in fine, transparent, yellowish prisms, which melt below 100° and resemble opianic acid in forming an anhydride.

Chloropianic acid, $(CH_3O)_2CHCl(COH)CO_2H$, is formed by the action of potassium chlorate on a hot solution of opianic acid in hydrochloric acid, and crystallizes from hot water in small prisms melting at 210°—211° (Prinz).

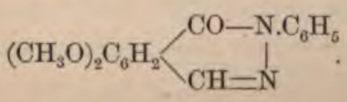
Bromopianic acid, $(CH_3O)_2C_6HBr(COH)CO_2H$, is prepared by adding bromine to a boiling solution of opianic acid (Prinz) and by triturating opianic anhydride with bromine (Wegscheider). It crystallizes from hot water in small, arborescent needles which melt at 204°.

Nitro-opianic acid, $(CH_3O)_2C_6H(NO_2)(COH)CO_2H$, is formed, together with nitrohemipinic acid, by the action of concentrated nitric acid on opianic acid. It is only slightly soluble in water, and crystallizes in lustrous yellow prisms, melting at 166°. Its salts are readily soluble in water and crystallize well.

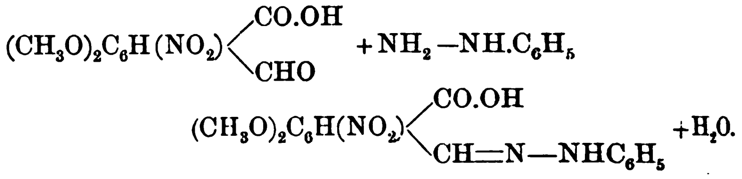
Opianylphenylhydrazide, $C_{16}H_{14}N_2O_3$, is obtained by mixing hot solutions of opianic acid, phenylhydrazine hydrochloride, and sodium acetate (Part III. p. 283):

$$C_{10}H_{10}O_5+C_6H_5N_2H_3=C_{16}H_{14}N_2O_3+2H_2O.$$

It crystallizes from alcohol in almost colourless needles, which melt at 175°, and are insoluble in alkalis, but dissolve in concentrated hydrochloric acid, from which solution they are precipitated by water. It is therefore a weak base, and is very stable, being unattacked by concentrated sulphuric acid even at 130°; it has probably the following constitution:



Phenylhydrazine nitro-opianic acid, $C_{16}H_{15}N_3O_6$, is formed in a similar manner, according to the equation:



$$(CH_3O)_2C_6H(NO_2)\begin{cases}CO.OH\\CHO\end{cases} + NH_2-NH.C_6H_5 = (CH_3O)_2C_6H(NO_2)\begin{cases}CO.OH\\CH{=}N-NHC_6H_5\end{cases} + H_2O.$$

It crystallizes in splendid, carmine-red needles, which melt at 184°, and form a red solution in alkalis. Acids convert it into *nitro-opianylphenylhydrazide*, $C_{16}H_{13}N_3O_5$, which crystallizes in yellow, silky needles, melting at 173°, is insoluble in alkalis, and behaves as a weak but stable base.[1]

When it is boiled with alcoholic potash, it decomposes into methyl alcohol and *nitromethylnoropianylphenylhydrazide*, $C_{15}H_{11}N_3O_5$, which has also been prepared from methylnoropianic acid.[2] This substance crystallizes in glittering, yellow plates, melting at 191°, and since it is a phenol, behaves as a weak acid.

Amido-opianylphenylhydrazide, $C_{16}H_{15}N_3O_3$, is obtained by the reduction of the nitro-compound with tin and hydrochloric acid. It crystallizes in fine needles, and oxidizes in the air to amidohemipinylphenylhydrazide.

2266 *Isonoropianic acid*, $C_6H_2(OH)_2(COH)CO_2H(CO_2H : OH : OH : COH\ 1 : 3 : 4 : 5)$, is formed when the following compound is heated to 170°—180° with hydrochloric acid. It is tolerably soluble in cold, readily in hot water, and crystallizes in yellowish needles, which melt with decomposition a few degrees above 240°. Its aqueous solution is coloured yellow by alkalis and dark green by ferric chloride, this colour being instantly changed to reddish violet by the addition of ammonia. It reduces ammoniacal silver solution in the cold, and Fehling's solution on boiling.[3]

Methylisonoropianic acid or *Aldehydovanillic acid*, $C_8H_2(OCH_3)(OH)COH(CO_2H)$, is formed, together with vanillin, when vanillic acid is heated with caustic soda and chloroform. It is readily soluble in alcohol, very slightly in cold, somewhat more readily in boiling water, from which it crystallizes in fine silky needles, which melt at 221°—222°. As an aldehydo-acid it combines with acid sodium sulphite; caustic soda colours the solution an intense yellow, while ferric chloride produces a dirty reddish violet colouration.

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[1] Liebermann, *Ber. Deutsch. Chem. Ges.* xix. 763.
[2] Elbel, *ibid.* xix. 2306.
[3] Mendelsohn and Tiemann, *ibid.* x. 393.

Its constitution follows from the fact that, in the synthesis of aldehydes or aldehydo-acids from phenols by means of chloroform, the aldehyde group always takes either the ortho- or para-position with regard to the hydroxyl. Since the latter is occupied in vanillic acid, the aldehyde group must lie next the hydroxyl, and the two groups are thus found in aldehydovanillic acid in the same relation as in salicylaldehyde—a view which is confirmed by its behaviour towards caustic soda and ferric chloride.[1]

As a phenol it forms two series of salts.[2]

Methyl aldehydovanillate, $C_6H_2(OCH_3)OH(COH)CO_2.CH_3$, is prepared by heating the acid with caustic potash, wood-spirit and methyl iodide, and forms yellow needles, which melt at 134°—135°, and are soluble in carbonates of the alkalis.

Isopianic acid, $C_6H_2(OCH_3)_2(COH)CO_2H$. The methyl ether of this compound is formed together with the foregoing compound. It crystallizes from boiling water in fine needles, which melt at 98°—99°, and are insoluble in the alkali carbonates. It is readily saponified by hot caustic potash solution. The free acid, which is precipitated by acids from this product, crystallizes from water in fine needles, melting at 210°—211°, which give no colouration with caustic soda or ferric chloride. It forms a slightly soluble compound with acid sodium sulphite.[3]

Quercimeric acid, $C_8H_6O_5+H_2O$. This substance, which is very similar to isonoropianic acid, was obtained by Hlasiwetz and Pfaundler by fusing quercitin with caustic potash. It forms crystalline granules or small prisms, is readily soluble in water, and reduces Fehling's solution and salts of silver. Ferric chloride produces a blue colouration in the aqueous solution, and an alkaline solution turns red in the air. On further fusion with potash protocatechuic acid is formed.[4]

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[1] *Ber. Deutsch. Chem. Ges.* ix. 1278.

[2] Mendelsohn and Tiemann, *ibid.* x. 395.

[3] *Ibid.* x. 397.

[4] *Jahresber.* 1864, 560.

DIHYDROXYPHTHALIC ACIDS, $C_6H_2(OH)_2(CO_2H)_2$.

2267 *Hemipinic acid* or *Dimethoxyorthophthalic acid*, $C_6H_2(OCH_3)_2(CO_2H)_2$, is, as already mentioned, a product of the oxidation of opianic acid, and has also been obtained by the oxidation of the alkaloids contained in opium, oxynarcotin and narceïn.[1] It is readily soluble in alcohol, very slightly in cold, more freely in boiling water, from which it crystallizes in colourless, distorted prisms with acute basal planes, containing two molecules of water which are lost below 100°. The anhydrous acid melts at 180°, and sublimes in lustrous plates, resembling those of benzoic acid (Wöhler). Crystals containing half a molecule of water are obtained by the spontaneous evaporation of its solution, while those deposited from a supersaturated solution contain one molecule (Matthiessen and Foster). It has a faint acid and slightly astringent taste, is decomposed into carbon dioxide and dimethylcatechol on heating with soda-lime, and is converted into rufiopin by hot sulphuric acid. Dilute hydrochloric acid decomposes it at 160°—170° into methyl chloride, carbon dioxide, isovanillic acid and protocatechuic acid (Wegscheider). Its aqueous solution is coloured yellowish brown by ferric chloride, and gives a white precipitate with lead acetate.

Normal potassium hemipinate, $C_{10}H_8O_6K_2$, is very soluble in water and does not easily crystallize.

Acid potassium hemipinate, $C_{10}H_9O_6K$, forms thick, six-sided tablets, which are readily soluble in water and alcohol, and have an acid reaction.

Normal silver hemipinate, $C_{10}H_8O_6Ag_2$, is a white precipitate, insoluble in water.

Acid a-methyl hemipinate, $C_6H_2(OCH_3)_2(CO_2.CH_3)CO_2H + H_2O$ ($OCH_3 : OCH_3 : CO_2CH_3 : CO_2H = 4 : 3 : 2 : 1$), is prepared by oxidizing methyl opianate with potassium permanganate, and crystallizes from hot water in lustrous, narrow, flat needles, which readily effloresce and when completely dehydrated melt at 121°—122°. Its solution gives a yellowish brown precipitate with ferric chloride.

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[1] Beckett and Wright, *Journ. Chem. Soc.* 1876, i. 461.

Acid β-methyl hemipinate, $C_6H_2(OCH_3)_2(CO_2H)CO_2.CH_3$ (4 : 3 : 2 : 1), is formed by passing hydrochloric acid into a solution of hemipinic acid in methyl alcohol. It is readily soluble in water and crystallizes from alcohol in arborescent needles or stellate groups of prisms, and from benzene or chloroform in rhombic tablets, which melt at 137°—138°. Its solution is not precipitated by ferric chloride (Wegscheider).

Acid ethyl hemipinate, $2C_6H_2(OCH_3)_2(CO_2.C_2H_5)CO_2H + 3H_2O$, was prepared by Anderson by passsing hydrochloric acid into the alcoholic solution of the acid. It is also formed by heating hemipinic anhydride with 90 per cent. alcohol (Matthiessen and Wright) and crystallizes from hot water in fascicular groups of needles, melting at 141°—142° (Wegscheider). Its solution is precipitated by ferric chloride, so that it corresponds to the α-methyl ether, and not, as might have been expected from its formation, to the β-compound.

Hemipinic anhydride, $C_{10}H_8O_5$, is formed when the acid is heated for an hour to 180° (Beckett and Wright), by the action of phosphorus pentachloride on the acid (Prinz) and by the distillation of the methyl ether (Wegscheider). It crystallizes from absolute alcohol, benzene, and xylene in lustrous needles, which melt at 167° and readily sublime. On heating with zinc dust and glacial acetic acid it is reduced to ψ-meconin (Salomon).

2268 *Nitrohemipinic acid*, $C_6H(NO_2)(OCH_3)_2(CO_2H)_2 + H_2O$, is best prepared by boiling nitro-opianic acid with pure nitric acid. It is also formed when meconin or ψ-meconin is heated under pressure with nitric acid (Salomon), and crystallizes from hot water in hard, yellow, vitreous prisms which lose water on heating, melt at 155°, and are converted into the anhydride at 160°—165°; the latter crystallizes from benzene in compact, light yellow prisms, and melts at 145°.[1]

Amidohemipinic acid, $C_6H(NH_2)(OCH_3)_2(CO_2H)_2$, was first prepared from its anhydride and was then obtained by Grüne by reducing nitrohemipinic acid with caustic soda and ferrous sulphate. The free acid is only known in its aqueous solution, which is coloured yellow, showing a fine green fluorescence, has an acid reaction and decomposes on evaporation.

Barium amidohemipinate, $C_{10}H_9NO_6Ba$, is obtained by boiling the anhydride with baryta water; it is a golden coloured crystalline powder, which dissolves in dilute acids, but is insoluble in water.

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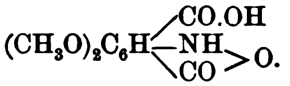
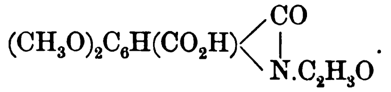
[1] Grüne, *Ber. Deutsch. Chem. Ges.* xix. 2299.

Anhydro-amidohemipinic acid was prepared by Prinz by the action of an acid solution of stannous chloride on a boiling solution of nitro-opianic acid and was named *azo-opianic acid.*[1] Liebermann then pointed out that this substance is probably the anhydride or anthranil of amidohemipinic acid:[2]



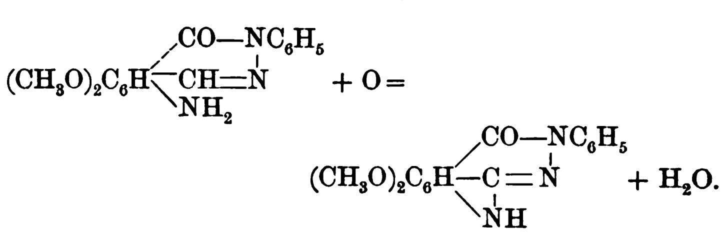
$$(CH_3O)_2C_6H\left\langle\begin{matrix}CO.OH \\ \begin{matrix}NH \\ CO\end{matrix}\Big\rangle O\end{matrix}\right.$$

The accuracy of this view was proved by Grüne. It crystallizes from alcohol in fine, colourless needles, which melt at 200° with decomposition. When its solution in concentrated hydrochloric acid is evaporated, the hydrochloride separates in stellate groups of prisms, which lose their hydrochloric acid on drying. Its potassium salt, $(CH_3O)_2CH(CONH)CO_2K$, is a crystalline powder, insoluble in alcohol. When it is boiled with acetic anhydride and anhydrous sodium acetate the acetyl-compound is formed, and crystallizes in needles which form an aqueous solution possessing a blue fluorescence. It readily decomposes with formation of free acetic acid, and has the following constitution:



$$(CH_3O)_2C_6H(CO_2H)\left\langle\begin{matrix}CO \\ | \\ N.C_2H_3O\end{matrix}\right. .$$

Amidohemipinylphenylhydrazide is formed by the continued boiling of anhydro-amidohemipinic acid with alcohol, phenylhydrazine hydrochloride, and sodium acetate, and also by the oxidation of amido-opianylphenylhydrazide in the air:



$$(CH_3O)_2C_6H\left\langle\begin{matrix}CO-NC_6H_5 \\ \qquad | \\ CH=N \\ NH_2\end{matrix}\right. + O = (CH_3O)_2C_6H\left\langle\begin{matrix}CO-NC_6H_5 \\ \qquad | \\ C=N \\ | \\ NH\end{matrix}\right. + H_2O.$$

It crystallizes from benzene or alcohol in small, vitreous, honey-yellow crystals belonging to the tetragonal system, which melt at 222.°[3]

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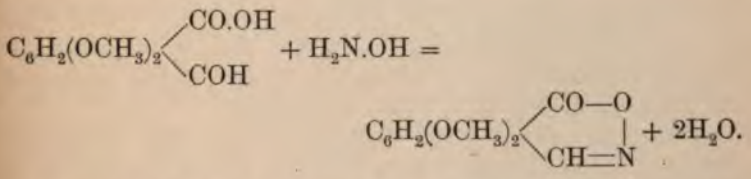
[1] *Journ. Prakt. Chem.* [2] xxiv. 362.
[2] *Ber. Deutsch. Chem. Ges.* xix. 351.
[3] Liebermann, *ibid.* xix. 2275.

Diazohemipinic acid, $(CH_3O)_2C_6H(CO_2H)<\substack{N=N\\ CO-O}>$, is obtained by the addition of hydrochloric acid to a cooled solution of sodium amidohemipinate and sodium nitrite. It forms a light yellow, crystalline powder, which explodes by percussion or on heating. When it is dissolved in warm hydrochloric acid, the chloride, $(CH_3O)_2C_6H(CO_2H)_2N_2Cl$, separates on cooling in long needles, which are instantly converted by water into their constituents (Grüne).

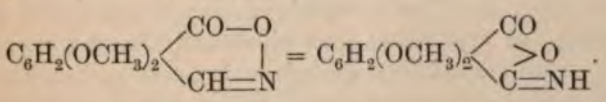
Opianoxime anhydride, $C_{10}H_9NO_4$, is formed when an alcoholic solution of opianic acid and hydroxylamine hydrochloride is allowed to stand:



$$C_6H_2(OCH_3)_2\left\langle\begin{array}{l}CO.OH\\ COH\end{array}\right. + H_2N.OH = C_6H_2(OCH_3)_2\left\langle\begin{array}{l}CO-O\\ \qquad|\\ CH=N\end{array}\right. + 2H_2O.$$

It crystallizes from benzene in long needles, which on careful heating melt at 114°—115°, and are converted into acid ammonium hemipinate by boiling with water.[1]

Hemipinimide, $C_{10}H_9NO_4$. This compound, which corresponds to phthalimide, is formed when ammonium hemipinate is heated and when an alcoholic solution of opianic acid is boiled with hydroxylamine hydrochloride, the foregoing compound being first formed and then undergoing an intramolecular change, which also occurs when it is rapidly heated to 117°; the temperature rises suddenly to 260°, and the liquid solidifies on cooling to crystals of hemipinimide:



$$C_6H_2(OCH_3)_2\left\langle\begin{array}{l}CO-O\\ \qquad|\\ CH=N\end{array}\right. = C_6H_2(OCH_3)_2\left\langle\begin{array}{l}CO\\ \quad >O\\ C=NH\end{array}\right. .$$

It crystallizes from hot water in splendid needles, which melt at 228°—230° and readily sublime. Its aqueous solution has a fine blue fluorescence. When it is triturated with a cold alcoholic solution of potash, *potassium hemipinimide*, $C_{10}H_8O_4(NK)$, is formed as a crystalline powder, whose aqueous solution gives a white precipitate of *silver hemipinimide*, $C_{10}H_8O_4(NAg)$, with silver nitrate.

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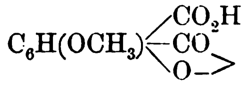
[1] Liebermann, *Ber. Deutsch. Chem. Ges.* xix. 2923.

Ethyl hemipinimide, $C_{10}H_8O_4(NC_2H_5)$, is obtained when the potassium compound is heated to 150° with ethyl iodide. It crystallizes from hot water or benzene in needles, which melt at 96°—98°. The solution also shows a blue fluorescence.[1]

2269 *Methylnorhemipinic acid*, $C_6H_2(OCH_3)OH(CO_2H)_2 + 2H_2O$ (4 : 3 : 2 : 1), is formed by heating hemipinic acid with hydriodic acid for a short time,[2] and by heating acid *a*-methyl hemipinate with hydrochloric acid. It forms warty crystals, which are readily soluble in water and alcohol. It reduces ammoniacal silver solution in the cold and Fehling's solution on heating, gives a deep blue colouration with ferric chloride, and melts at 152°—155° with decomposition. It separates from ether as an anhydrous powder, which melts at 223°—225° with evolution of gas (Wegscheider). On dry distillation it decomposes into isovanillic acid and carbon dioxide, and is converted into protocatechuic acid by fusion with potash.

In its preparation from hemipinic acid, the compound $C_9H_6O_4 + 2H_2O$ is formed as a by-product. It crystallizes in lustrous prisms or thin tablets, which melt at 148°. Its aqueous solution is coloured lilac by ferric chloride.

This substance, which Liechti named *opinic acid*, might be methylnorhemipinic anhydride, but this is considered doubtful by Beckett and Wright since it contains water of crystallization, and they assume that it corresponds to salicylide and has the following constitution:



$$C_6H(OCH_3)\begin{cases} CO_2H \\ CO \\ O- \end{cases}\!\!\!>$$

Nitromethylnorhemipinic acid, $C_6H(NO_2)(OCH_3)OH(CO_2H)_2$, is formed when methylnorhemipinic acid is evaporated with dilute nitric acid, and crystallizes from alcohol in almost white, silky needles, which are readily soluble in water, and melt at 220°.[3]

Amidomethylnorhemipinic acid, $C_6H(NH_2)(OCH_3)OH(CO_2H)_2$, is not known in the free state; its barium salt separates in lustrous, dull yellow plates when the anhydro-acid is boiled with baryta water.

Anhydro-amidomethylnorhemipinic acid, $(CH_3O)(OH)C_6H(CO_2H){<}\substack{CO\\NH}{>}O$, is prepared by adding stannous chloride and hydrochloric acid to a boiling, saturated solution of nitromethylnoropianic acid, and crystallizes in silky needles, which melt at 174°—175° with decomposition. On boiling with acetic anhydride and sodium acetate, the diacetyl compound is formed:

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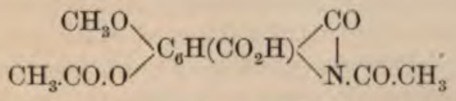
[1] Liebermann, *Ber. Deutsch. Chem. Ges.* xix. 2287.
[2] Beckett and Wright, *loc. cit.*; Liechti, *Ann. Chem. Pharm.* Suppl. vii. 149.
[3] Elbel, *Ber. Deutsch. Chem. Ges.* xix. 2306.



$$\left.\begin{array}{r}CH_3O\\CH_3.CO.O\end{array}\right>C_6H(CO_2H)\left<\begin{array}{l}CO\\ |\\N.CO.CH_3\end{array}\right.$$

It crystallizes in needles, melting at 205°, and yields a solution in alcohol which has a blue fluorescence. Acetic anhydride is set free on standing, the monoacetyl derivative, $C_6H(OCH_3)(OC_2H_3O)(CO_2H)(CONH)$, being formed. This body melts at 198° and does not form a fluorescent solution in alcohol.

Isohemipinic acid, $C_6H_2(OCH_3)_2(CO_2H)_2$, is formed by the oxidation of methyl isopionate with potassium permanganate. The methyl ether is thus obtained, which crystallizes in needles melting at 167°, and yields the acid on saponification. The latter forms white needles, which are scarcely soluble in cold, more readily in hot water, and melt at 245°—246° (Mendelsohn and Tiemann).

2270 *Dihydroxyisophthalic acid*, or *Resorcinoldicarboxylic acid*, $C_6H_2(OH)_2(CO_2H)_2$. When resorcinol is heated with caustic soda and chloroform, *dihydroxyisophthalaldehyde*, $C_6H_2(OH)_2(COH)_2$, is formed, which is almost insoluble in cold water, but dissolves readily in alcohol and ether, from which it is removed by agitation with acid sodium sulphite without forming a difficultly soluble compound. It crystallizes from hot water in long, strongly refractive needles, which melt at 127° and readily sublime. It forms a yellow solution in alkalis. On fusion with caustic potash resorcinoldicarboxylic acid is formed; this crystallizes from water in fine, white needles, which decompose on heating into resorcinol and carbon dioxide.[1] Its constitution has not been accurately determined, but the position of the side-chains is probably $OH:OH:CO_2H:CO_2H = 1:3:4:6$, since in this arrangement the carboxyls stand in both the ortho- and the para-relation to the hydroxyls.

Dihydroxyterephthalic acid, $(OH:OH:CO_2H:CO_2H=1:4:2:5)$. This body, which is also known as *quinoldicarboxylic acid*, is obtained by passing air into an alkaline solution of succinosuccinic ether (Part II. p. 190; III. p. 146) and decomposing the product with sulphuric acid.[1] It may also be readily prepared by saponifying the ether, and crystallizes from hot water in brownish yellow, hair-like needles, but from alcohol in deep yellow plates, while it separates from ether in rhombic tablets or prisms, which are coloured greenish yellow and show a light blue fluorescence. A hot supersaturated solution, however, first deposits asymmetric white and green crystals, the latter of which are less acutely pointed than the former. On further cooling the rhombic prisms appear and replace the asymmetric crystals when the solution is again gently warmed. If, however, the latter are isolated, the white plates are converted on cooling into the green, which again become white on warming, so that by alternate heating and cooling the same crystal can be obtained in either modification an indefinite number of times. Since the shape of the crystal alters with the colour, it can be made to present the appearance of a concertina, alternately elongated and compressed by causing the changes of temperature to follow one another rapidly.[2]

---

[1] Lewy and Tiemann, *Ber. Deutsch. Chem. Ges.* x. 2210.

The aqueous solution of the acid shows a faint emerald green fluorescence, while that of the alcoholic solution is light blue; it is coloured a pure deep blue by ferric chloride. When rapidly heated the acid decomposes with formation of quinol and other products.[3]

Normal sodium dihydroxyterephthalate, $C_6H_4O_2(CO_2Na)_2 + 2H_2O$, crystallizes on the spontaneous evaporation of its aqueous solution, in flat, light brown prisms.

Acid sodium dihydroxyterephthalate, $C_6H_4O_2(CO_2Na)CO_2H + 2H_2O$, forms light yellow, lustrous prisms.

Basic sodium dihydroxyterephthalate, $C_6H_2(ONa)_2(CO_2Na)_2 + 12H_2O$. The acid dissolves in caustic soda forming a deep yellow solution with a strong green fluorescence; on the addition of very concentrated caustic soda the basic salt separates in large transparent crystals, which possess a large number of faces and appear a faint greenish yellow by transmitted, but light blue by reflected light.

2271 *Diethyl dihydroxyterephthalate*, $C_6H_4O_2(CO_2.C_2H_5)_2$, is formed by the addition of bromine to a solution of succinosuccinic ether in carbon disulphide,[4] and by the action of sodium on an ethereal solution of dibromaceto-acetic ether,[5] $CH_3.CO.CBr_2.CO_2.C_2H_5$. The latter formation corresponds to that of succinosuccinic ether from monobromaceto-acetic ether. It crystallizes from ether in short, thick prisms or long flat needles, and from benzene in rectangular, rhombic tablets, which have the colour of uranium glass and show a light blue fluorescence. It melts at 133°—133·5° and sublimes at a higher temperature in lustrous, green, flat plates possessing a beautiful blue fluorescence. Its alcoholic solution is coloured bluish green by traces of ferric chloride. It dissolves in alkalis forming a deep yellow solution, with which a concentrated solution of an alkali produces a deep orange-red precipitate.

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[1] Herrmann, *Ber. Deutsch. Chem. Ges.* x. 111.

[2] Lehmann, *Zeitsch. Kryst.* x. 3; Herrmann, *Ber. Deutsch. Chem. Ges.* xix. 2229.

[3] Herrmann, *Ann. Chem. Pharm.* ccxi. 335.

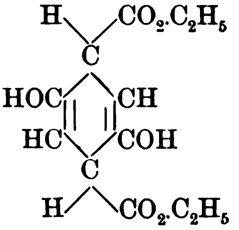
[4] Herrmann, *ibid.* ccxi. 372; *Ber. Deutsch. Chem. Ges.* xvi. 1411; Duisberg, *ibid.* xvi. 133; Ebert, *Ann. Chem. Pharm.* ccxxix. 45.

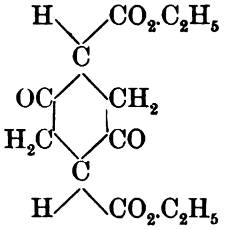
[5] Wedel, *ibid.* ccxix. 71.

Diethyl diacetoxyterephthalate, $C_6H_2(OCO.CH_3)_2(CO_2.C_2H_5)_2$, is prepared by heating the ethyl ether with acetyl chloride, and crystallizes from alcohol in colourless, lustrous plates, which melt at 115° (Wedel).

Monethyl dihydroxyterephthalate, $C_6H_2(OH)_2(CO_2.C_2H_5)CO_2H$. When the diethyl ether is dissolved in dilute caustic potash and the unattacked portion removed after some time by acetic acid, barium chloride precipitates the barium salt of the acid ether from the filtrate; this salt can readily be recrystallized from hot water, and hydrochloric acid added to its solution precipitates the mono-ethyl ether of dihydroxyterephthalic acid. It is a strong monobasic acid, crystallizes from hot water in fine, yellow needles, and is deposited on the evaporation of its alcoholic solution in light yellow, transparent, vitreous prisms, which melt at 184°. Its solution is coloured bluish violet by ferric chloride.

If the diethyl ether is boiled with alcoholic hydrochloric acid and zinc, it is again reduced to succinosuccinic ether, which can therefore be regarded as the ether of a dihydroxydihydroterephthalic acid. The latter is formed in the first stage of the reaction, but immediately changes into the isomeric compound:[1]





The latter formula is rendered probable by the formation of the substance from bromaceto-acetic ether, $CH_3.CO.CHBr.CO_2.C_2H_5$, which occurs with elimination of hydrobromic acid; it also forms a di-imide, is converted into an oximido-compound by hydroxylamine (Baeyer), and yields both a phenylhydrazide and a diphenylhydrazide.[1] On the other hand it yields a diacetyl-compound on heating with acetyl chloride (Wedel), which is more readily obtained by adding sodium ethylate to its ethereal solution, a rose-coloured precipitate of $C_6H_4O_2Na_2(CO_2.C_2H_5)_2$ being formed, which is immediately converted by acetyl chloride into the compound $C_6H_4(OC_2H_3O)_2(CO_2.C_2H_5)_2$ (Baeyer). The latter compounds must be looked upon as derivatives of the dihydroxy-dihydroterephthalic acid into which succinosuccinic ether or quinonetetrahydrodicarboxylic acid so readily changes.

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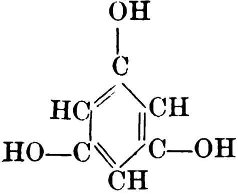
[1] *Ber. Deutsch. Chem. Ges.* xix. 428.

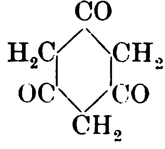
Dihydroxyterephthalic acid also probably exists in two forms, as *quinoldicarboxylic acid*, $C_6H_2(OH)_2(CO_2H)_2$, and as *quinonedihydrodicarboxylic acid*, $C_6O_2H_4(CO_2H)_2$, which readily change into one another. The latter formula is required by its formation from dibromaceto-acetic ether, while its whole behaviour corresponds to the former. It may be assumed that the green modification is the quinone-acid, while the colourless is the quinol derivative (Herrmann).

A similar case has been observed by Baeyer with regard to phloroglucinol, which forms a trioxime with hydroxylamine, the trihydroxybenzene being converted into triketohexhydrobenzene (Part III. p. 186.):[2]

Phloroglucinol.



Triketohexhydrobenzene.



Analogous cases have long been known to chemists; among the simplest are nitrous acid and cyanic acid, which are exceedingly unstable in the free state, but yield stable modifications of two kinds:

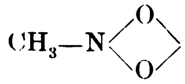
Methyl nitrite.

$CH_3—O—N=O$

Potassium cyanate.

$K—O—C\equiv N$

Nitromethane.



Methyl isocyanate.

$CH_3—N=C=O$

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[1] Knorr, *Ber. Deutsch. Chem. Ges.* xvii. 2055.

[2] *Ibid.* xviii. 3454 ; xix. 159, 1800.

The constitution of these compounds can therefore be represented with equal accuracy by different structural, or, as Laar[1] names them, tautomeric formulæ. The atoms are in continual motion within the molecule, and one form is converted into the other when the light and most rapidly moving atoms of hydrogen are more strongly attracted by one or other of the remaining atoms. If, however, the hydrogen be replaced by a heavier atom or molecule, the latter no longer escapes from the sphere of attraction, and the mobile form is converted into a stable one.

TRIHYDROXYPHTHALIC ACIDS, $C_6H(OH)_3(CO_2H)_2$.

2272 *Gallocarboxylic acid*, $C_8H_6O_7 + 3H_2O$, is formed, together with pyrogallolcarboxylic acid (p. 378), when pyrogallol or gallic acid is heated to 130° with ammonium carbonate. It requires 3,000 parts of water at 0° for solution, and crystallizes from hot water in very fine needles, which become anhydrous at 180° and melt above 270° with evolution of carbon dioxide. Dilute ferric chlorides colour its solution violet, while the concentrated reagent produces a greenish brown colouration. When heated in the air with water and an excess of calcium carbonate, the latter is coloured reddish violet, and when an ammoniacal solution of the acid is mixed with a solution of bicarbonate of calcium, a deep violet coloured precipitate is formed, which may therefore be obtained with spring water containing calcium carbonate.[2]

TETRAHYDROXYPHTHALIC ACIDS, $C_6(OH)_4(CO_2H)_2$.

2273 *Tetrahydroxyterephthalic acid.* When an ethereal or alcoholic solution of ethyl dihydroxyterephthalate is treated with anhydrous nitrogen trioxide, it is converted into *ethyl dihydroxyquinoneterephthalate*, $C_6O_2(OH)_2(CO_2 \cdot C_2H_5)_2$, crystallizing in yellow prisms, which are slightly soluble in cold water, alcohol and ether, more readily in chloroform. The solutions have a deep yellowish red colour. When the ether is heated with caustic soda, a basic salt of dihydroxyquinoneterephthalic acid is formed, and immediately decomposes on the addition of acids into carbon dioxide and *dihydroxyquinone*, $C_6O_2H_2(OH)_2$, which forms small, black-brown crystals. Nitranilic acid, $C_6O_2(NO_2)_2(OH)_2$, is always formed if dihydroxyterephthalic acid be submitted to the same treatment.

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[1] *Ber. Deutsch. Chem. Ges.* xviii. 648; xix. 730.

[2] Brunner and Senhofer, *Monatsh. Chem.* i. 468.

Ethyl tetrahydroxyterephthalate, $C_6(OH)_4(CO_2.C_2H_5)_2$, is obtained by passing sulphur dioxide into a faintly alkaline solution of the dihydroxyquinone ether, and crystallizes from hot chloroform in golden yellow plates, melting at 178°. It is converted by cold caustic soda solution into *sodium tetrahydroxyterephthalate*, $C_6(OH)_4(CO_2Na)_2$, which crystallizes in yellow prisms. On decomposition with sulphuric or hydrochloric acid, tetrahydroxyphthalic acid yields carbon dioxide and tetrahydroxybenzene, $C_6H_2(OH)_4$, which forms yellow needles, melting at 148°.[1]

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[1] Loewy, *Ber. Deutsch. Chem. Ges.* xix. 2385.

INDEX

INDEX.

A.

ACETBROMAMIDE, 113
Acetmetamidobenzoic acid, 248
Acetmetatoluide, 62
a-Acetmetaxylide, 407
s-Acetmetaxylide, 407
v-Acetmetaxylide, 406
Acetmethylparatoluide, 65
Acetometahydroxybenzidene acetate, 293
Acetortho-amidobenzoic acid, 239
Acetorthotoluide, 59
a-Acetorthoxylide, 406
v-Acetorthoxylide, 406
Acetoxime benzyl ether, 98
Acetparamidobenzoic acid, 253
Acetparatoluide, 66
Acetparaxylide, 407
Acetphthalimide, 464
Acetylbenzenylamidoxime 214
Acetylisovanillic acid, 354
Acetylmetahydroxybenzaldehyde, 293
Acetylopianic acid, 506
Acetylorthamidobenzaldehyde, 149
Acetylparahydroxybenzaldehyde, 295
Acetylparahydroxybenzidene acetate, 296
Acetylparamidobenzaldehyde, 150
Acetylsalicylic acid, 308
Acetyl salicylaldehyde, 288
Acetylsinapic acid, 377
Acetylvanillic acid, 353
Acetylvanillin, 347
Acid ammonium hippurate, 189
Acid ammonium phthalate, 456
Acid barium hydroxamate, 208
Acid barium orthosulphobenzoate, 268
Acid bariumphthalate, 457
Acid calcium benzarsenate, 277
Acid ethyl hemipinate, 511
Acid ethyl metasulphobenzoate, 271
Acid ethyl α-nitrophthalate, 474
Acid ethyl ν-nitrophthalate, 474
Acid metatoluidine oxalate, 61
Acid α-methyl hemipinate, 510
Acid β-methyl hemipinate, 511
Acid methyl sulphinidephthalate, 478
Acid paratoluidine oxalate, 64
Acid potassium benzarsenate, 277
Acid potassium benzhydroxamate, 208
Acid potassium benzophosphinate, 276
Acid potassium hemipinate, 510
Acid potassium sulphinidephthalate, 477
Acid potassium sulphoparahydroxybenzoate, 336
Acide quinique, 382
Acid silver sulphinidephthalate, 478
Acid sinapin sulphate, 375
Acid sodium benzhydroxamate, 208
Acid sodium dihydroxyterephthalate, 516
Addition products of isophthalic acid, 481
Addition products of phthalic acid, 469
Addition products of terephthalic acid, 486
Adjacent Dinitroparatoluidine, 71
Adjacent metadihydroxybenzoic acid, 360
Aes-cioxalic acid, 363
Aldehydes, 447
Aldehydovanillic acid, 508
Aldehydohydroxybenzoic acids, 491, 502
Alizaric acid, 450
Allyl benzoate, 162
Aloïsol, 402
Amarine, 140
Amarythrin, 428
Amido-anisic acid, 338
Amido-azotoluenes, 77
Amidobenzenyl-phenylene-amidine, 206
Amidobenzoic acid percyanide, 248
Amidobenzylamines, 120
Amido-derivatives of the xylenes, 405
Amidohemipinic acid, 511
Amidohemipinylphenylphydrazide, 512
Amido-isophthalic acid, 482
Amidomeconin, 501
Amidometa-azotoluene, 78
Amidometatoluic acids, 418

Amidomethylnorhemipinic acid, 514
Amido-opianylphenylhydrazide, 508
Amidortho-azotoluene, 77
β-Amido-orthocresol, 26, 51
γ-Amido-orthophenol, 26
Amido-orthotoluic acids, 415
Amido-ψ-meconin, 501
α-Amidoparacresol, 20
β-Amidoparacresol, 30
γ-Amidoparacresol, 30
Amidoparahydroxybenzoic acid, 335
α-amidoparatoluic acid, 421
Amidophenylmetabenzoglycocyamine, 253
Amidophthalic acids, 475
α-Amidophthalic acid, 475
v-Amidophthalic acid, 475
α-Amidosalicylic acid, 317
β-Amidosalicylic acid, 318
Amido-substituted benzylamines, 116
Amidosulphobenzoic acids, 275
Amidoterephthalic acid, 489
Amidotoluenes, 54
Amido-uramidobenzoyl, 242
Amidoxylenes, 405
Ammonium benzidene sulphate, 137
Ammonium benzoate, 160
Ammonium gallate, 368
Ammonium metahydroxybenzoate, 321
Ammonium parahydroxybenzoate, 328
Ammonium salicylate, 303
Ammonium terephthalate, 484
Amyg-dalaceæ, 131
Amygdalin, 130
Amyl benzoate, 162
Amyl hippurate, 191
Amyl orsellinate, 433
Amyl salicylate, 306
Anhydrides of parahydroxybenzoic acid, 331
Anhydro-amidohemipinic acid, 512
Anhydro - amidomethylnorhemipinic acid, 514
Anhydrobenzodiamidobenzene, 205
Anhydrous benzoic acetic acid, 167
Aniletic acid, 316
Anilido-ethoxytolu-quinone anilide, 49
Anilidohydroxytoluquinone, 49
Anilidohydroxytoluquinone anilide, 49
Aniline, 297
Aniline lourde spéciale, 56
Aniline oil, 55
Aniline orange, 31
Anis-amide, 333
Anis-anilide, 333
Anisbenzanishydroxylamine, 342
Anisbenzethylhydroxylamine, 340
Anisbenzhydroxamic acid, 340
Anis-dibenzhydroxylamine, 341
Anise alcohol, 284
Anisenyloxime compounds, 339
Anisethylbenzhydroxylamine, 341
Anishydroxamic acid, 339
Anisic acid, 329
Anisic acid, substitution products of, 336
Anisic anhydride, 332
Anisonitril, 334
Anisuric acid, 333
Anisyl chloride, 332
Anthranil, 240
Anthranilcarboxylic acid, 240
Anthranilic acid, 297
Antimony derivatives of toluene, 86
Archil, 42
Arsendiparatolyl chloride, 85
Arsendiparatolyl trichloride, 85
Arsenditolyl oxide, 85
Arsenic Compounds of Benzyl, 125
Arsenic derivatives of toluene, 84
Arsenobenzoic acid, 277
Arsenorthotolyl chloride, 85
Arsenorthotolyl dioxide, 86
Arsenorthotolyl oxide, 85
Arsenparatolyl chloride, 84
Arsentolyl oxide, 85
Arsentribenzoic acid, 278
Arsentritolyl dichloride, 85
Asymmetric diamido-azotoluene, 80
Asymmetric dibenzyl thiocarbamide, 124
Asymmetric dibenzyl urea, 123
Asymmetric ethylbenzoyl urea, 178
Asymmetric metadihydroxybenzoic acid, 359
Asymmetric diphenylbenzenylamidine, 204
Azo-aceto-acetic benzoic acid, 267
Azobenzenesalicylic acid, 319
Azobenzoic acids, 265
Azo-derivatives of benzoic acid 265
Azo-derivatives of toluene, 75
Azomalonic-benzoic acid, 268
Azonitromethanebenzoic acid, 267
Azo-orcin, 52
Azophenylmethyl, 181
Azo-opianic acid, 512
Azotoluenes, 75
α-Azotoluidine, 79
β-Azotoluidine, 79
Azoxybenzoic acids, 265
α-Azoxytoluidine, 78
β-Azoxytoluidine, 79

B.

BADIANIC ACID, 329
Barbatic acid, 402, 435
Barium amidohemipinate, 511
Barium benzoate, 161
Barium benzylsulphonate, 108
Barium chlorobenzylsulphonate, 108
Barium diamidobenzoate, 259
Barium α-dinitrobenzoate, 234
Barium β-dinitrobenzoate, 234
Barium γ-dinitrobenzoate, 234

Barium δ-dinitrobenzoate, 235
Barium ε-dinitrobenzoate, 235
Barium dinitrosalicylate, 317
Barium gallate, 369
Barium hippurate, 189
Barium homohydroxysalicylate, 438
Barium isophthalate, 479
Barium lecanorate, 434
Barium meconinate, 500
Barium metabromobenzoate, 224
Barium metahydroxybenzoate, 321
Barium metanitrobenzoate, 231
Barium methylnoropianate, 503
Barium opianate, 504
Barium opianylsulphite, 507
Barium ornithurate, 193
Barium orsellinate, 432
Barium orthobromobenzoate, 223
Barium orthonitrobenzoate, 230
Barium parabromobenzoate, 224
Barium parahydroxybenzoate, 328
Barium paranitrobenzoate, 232
Barium para-orsellinate, 436
Barium protocatechuate, 352
Barium pyrogallolcarboxylate, 379
Barium quinate, 384
Barium salicylaldehyde, 287
Barium salicylate, 303
Barium terephthalate, 484
Basic barium nitroparahydroxybenzoate, 335
Basic copper potassium salicylate, 304
Basic copper quinate, 384
Basic lead pyro-gallolcarboxylate, 379
Basic sodium dihydroxyterephthalate, 516
Benzaldehyde, 129
Benzaldehyde-green, 135
Benzaldehyde oxyiodide, 137
Benzaldoxime, 139
Benzamic acid, 246
Benzamide, 172, 199
Benzamide hydrochloride, 174
Benzanilide, 174
Benzanilidimidochloride, 203
Benzanisbenzhydroxylamine, 341
Benzanishydroxamic acid, 340
Benzarsene chloride, 277
Benzarsene iodide, 277
Benzarsenic acids, 277
Benzarsenious acid, 277
Benzdianishydroxylamine, 342
Benzene, 297
Benzenyl alcohol, 194
Benzenyl amidines, 195
Benzenylamidophenate, 206
Benzenylamidothiophenate, 206
Benzenylamidoxime, 212
Benzenylamidoximemetacarboxylic acid, 480
Benzenylamidoximeparacarboxylic acid, 485
Benzenylazoximebenzenylcarboxylic acid, 468
Benzenylazoxime carbinol, 215
Benzenylazoxime propenylcarboxylic acid, 215
Benzenyl compounds, 194
Benzenylethoxime chloride, 213
Benzenylethenylazoxime, 214
Benzenyl ethyl ether, 196
Benzenyloxime compounds, 207
Benzenyloximic acid, 208
Benzenyl triacetate, 196
Benzenyl tribromide, 196
Benzenyl trichloride, 195
Benzenyltrichlorophosphoryl chloride, 311
Benzethylanishydroxylamine, 341
Benzethylbenzhydroxylamine, 209
Benzhydroxamic acid, 208
Benzhydroxamide, 212
Benzhydroxylamine, 207
Benzidene-acetamide, 143
Benzidene-aniline, 140
Benzidene-aniline cyanhydrate, 141
Benzidene benzoate, 163
Benzidene benzobromohydrin, 170
Benzidene benzochlorohydrin, 169
Benzidene compounds, 136
Benzidene diacetate, 137
Benzidene dibromide, 136
Benzidene dichloride, 136
Benzidene dichlorochromic acid, 6
Benzidene diethyl ether, 136
Benzidene di-iodide, 137
Benzidenedimethylparadiamidobenzene, 142
Benzidenediphenylhydrazine, 141
Benzidenedi-ureïde, 143
Benzidene-orthodiamidobenzene, 141
Benzideneparadiamidobenzene, 142
Benzidenephenylamine hydrochloride, 143
Benzidenephenylhydrazine, 141
Benzidenephenyldiamine, 142
Benzidene sulphide, 138
Benzidenetetra-ureïde, 143
Benzidenetri-ureïde, 143
Benzidene ureïdes, 143
Benzidene urethane, 143
Benzidenoxime, 139
Benzimido-acetic ether, 201
Benzimido-amide, 202
Benzimido-ethers, 200
Benzimido-ethyl ether, 201
Benzimido-isobutyl ether, 201
Benzimido-thiobenzyl ether, 202
Benzimido-thio-ethyl ether, 201
Benzoene, 3
Benzoène monochloré, 7
Benzoic acid, 7, 108, 151, 297, 383
Benzoic acid, azo-derivatives of, 265
Benzoic acid, nitro-substitution products of, 227
Benzoic acid, salts and ethers of, 160
Benzoic anhydride, 166
Benzoleic acid, 159

Benzonitril, 122, 197
Benzonitril and its derivatives, 197
Benzophosphine chloride, 276
Benzophosphinic acid, 275
Benzolorthoalcoholsäme, 442
Benzortho-amidobenzoic acid, 239
α-benzothio-aldehyde, 138
β-benzothio-aldehyde, 138
γ-benzothio-aldehyde, 139
Benzo-trichloride, 195
Benzoxamidine, 213
Benzoyl, 285
Benzoyl acetyl oxide, 167
Benzoylaniline, 174
Benzoylanthranil, 241
Benzoylazobenzene, 180
Benzoylbenzenylamidoxime, 214
Benzoyl-benzoic acid, 458
Benzoylbenzoximic acid, 209
Benzoyl bromide, 169
Benzoyl chloride, 168
Benzoyl derivatives of amines and amido-bases, 174
Benzoyl dioxide, 167
Benzoyldiphenylamine, 175
Benzoyldiphenylhydrazine, 181
Benzoyl disulphide, 171
Benzoyl ethylbenzhydroxamate, 209
Benzoyl fluoride, 170
Benzoyl-glycollic acid, 165
Benzoyl group, 128
Benzoylguanidine, 243
Benzoylguanidine, nitrate, 243
Benzoyl, halogen compounds of, 168
Benzoylhelicin, 289
Benzyl hydrosulphide, 138
Benzoyl iodide, 170
Benzoyl-lactic acid, 165
Benzoylmethylaniline, 175
Benzoylmethylpyrogallol dimethyl ether, 164
Benzoylnitranilines, 175
Benzoyl, nitrogen compounds of, 172
Benzoylornithine, 193
Benzoylorthotoluide, 175
Benzoyl oxide, 166
Benzoyl, oxides of, 166
Benzoylparatoluide, 175
Benzoyl peroxide, 167
Benzoylphenylhydrazine, 179
Benzoylpropylpyro - gallol dimethyl ether, 164
Benzoylpyro-gallol dimethyl ether, 164
Benzoylsalicin, 282
Benzoyl salicylaldehyde, 288
Benzoylsalicylamide, 312
Benzoylsalicylnitril, 313
Benzoyl sulphide, 171
Benzoylsulphimide, 269
Benzoyl, sulphur compounds of, 170
Benzoyl thiocyanate, 172
Benzoyl thio-urea, 179
Benzoyl urea, 178
Benzoylvanillic acid, 353
Benzyl, 89
Benzylacetamide, 121
Benzyl acetate, 97
Benzyl alcohol, 7, 89 ; properties, 93 ; substitution products of, 98
Benzylamidine, 202
Benzylamine, 112 ; properties, 113
Benzylamine hydrochloride, 113, 114
Benzylamine nitrite, 114
Benzylamines, 110
Benzylamines, amido-substituted, 116
Benzylamines, substitution products of, 118
Benzylammonium benzylcarbamate, 113, 114
Benzylaniline, 117
Benzyl, arsenic compounds of, 125
Benzyl benzoate, 162
Benzylbenzoyl thio-urea, 179
Benzyl bromide, 97
Benzyl bromophenyl ether, 95
Benzyl carbamate, 123
Benzyl-carbimide, 122
Benzyl chloride, 7, 96
Benzyl chlorophenyl ether, 95
Benzylcyananmide, 121
Benzylcyanuramide, 121
Benzyl-Derivatives of the Acid-Amides and Allied Bodies, 121
Benzyldimethylselenine tri-iodide, 110
Benzyldimethylsulphine iodide, 106
Benzyl dimethylsulphine platinichloride, 107
Benzyl dioxysulphide, 107
Benzyl diphenylamine, 117
Benzyl diselenide, 109
Benzyl disulphide, 107
Benzyl, ethereal salts of, 96
Benzyl ethers, 94
Benzylethoxyl chloride, 100
Benzyl ethyl ether, 94
Benzyl ethyl sulphide, 106
Benzyl group, 89
Benzyl hydrosulphide, 105
Benzylhydroxyammonium chloride, 98
Benzyl iodide, 97
Benzyl-isocyanate, 122
Benzyl isocyanurate, 122
Benzyl isothiocyanate, 122
Benzylmetamine, 121
Benzyl methyl ether, 94
Benzyl mercaptan, 105
Benzyl mustard oil, 122
Benzyl nitrate, 97
Benzyl, nitrogen bases of, 110
Benzyl orthocresyl ether, 95
Benzyl oxalate, 98
Benzyl oxide, 94
Benzyl oxysulphide, 107
Benzyl paracresyl ether, 95
Benzylphenylamine, 117
Benzyl phenyldimethylammonium chloride, 117
Benzyl phenyl ether, 95

Benzylphosphine, 124
Benzylphosphonium iodide, 124
Benzylquinol, 96
Benzylsalicylic acid, 306
Benzyl salicylaldehyde, 287
Benzylselenic acid, 109
Benzyl selenide, 109
Benzyl, selenium compounds of, 109
Benzyl selenocyanate, 123
Benzyl, silicon compounds of, 127
Benzyl sulphide, 106
Benzylsulphonamide, 109
Benzylsulphonic acid, 108
Benzylsulphonic chloride, 108
Benzyl, sulphur compounds of, 105
Benzyl thiocarbamide, 124
Benzyl thiocyanate, 122
Benzyl thiobenzoate, 171
Benzyl urea, 123
Benzyl urethane, 123
Beta-orcinol, 402
Boron and Silicon derivatives of Toluene, 87
Boron disalicylic acid, 304
Bromamidobenzoic acids, 255
Bromanisic acid, 336
Bromine substitution products, 41
Bromine substitution products of toluene, 10
Bromobenzidenedichlorochromyl chloride, 11
Bromobenzylbenzoate, 170
Bromogallic acid, 370
Bromomalophthalic acid, 470
Bromomeconin, 500
Bromometacresol, 27
α-Bromometatoluic acid, 417
β-Bromometatoluic acid, 417
α-Bromometaxylene, 394
s-Bromometaxylene, 394
α-Bromometaxylenol, 401
Bromonitrobenzoic acids, 236
Bromonitrotoluenes, 19
Bromoparacresol, 29
Bromoparahydroxybenzaldehyde, 296
α-Bromoparatoluic acid, 420
β-Bromoparatoluic acid, 420
Bromoparaxylene, 395
α-Bromophthalic acid, 472
v-Bromophthalic acid, 472
Bromopianic acid, 507
Bromoprotocatechuic acid, 356
α-Bromoresorcylic acid, 359
γ-Bromoresorcylic acid, 361
Bromorthocresol, 25
α-Bromorthotoluic acid, 415
β-Bromorthotoluic acid, 415
α-Bromorthoxylene, 393
Bromosalicylaldehyde, 292
α-Bromosalicylic acid, 314
β-Bromosalicylic acid, 314
Bromosulphobenzoic acids, 274
Bromoterephthalic acid, 488
Bromotoluidines, 68
Butyl benzoate, 162
Butyl hippurate, 191

C.

Caffeol, 281
Calcium benzarsenite, 278
Calcium benzoate, 160
Calcium dibenzarsenite, 278
Calcium difluorbenzoate, 227
Calcium gallate, 369
Calcium hippurate, 189
Calcium isophthalate, 479
Calcium metachlorobenzoate, 220
Calcium metahydroxybenzoate, 321
Calcium metatoluate, 416
Calcium ornithurate, 193
Calcium orthochlorobenzoate, 218
Calcium orthotoluate, 414
Calcium parachlorobenzoate, 221
Calcium parahydroxybenzoate, 328
Calcium paratoluate, 419
Calcium phthalate, 457
Calcium piperonate, 356
Calcium pyrogallolcarboxylate, 379
Calcium quinate, 382, 384
Calcium salicylate, 303
Calcium terephthalate, 484
Cantharene, 391
Carbanilamide, 246
Carbanilidic acid, 246
Carbimidamidobenzoic acid, 250
Carbimidamidobenzoyl, 242
Carbohydrokinonic acid, 350
Carbonyl chloride, 462
Carbonyl dibenzenylamidoxime, 215
Carbotriphenyltriamine, 204
Carboxamidocyanamidobenzoyl, 241
Carboxamidobenzoic acid, 251
Carboxylcyanamidobenzoyl, 241
Catechol, 36
Chloranisic acid, 336
Chloramidobenzoic acids, 254
Chlorine substitution products, 41
Chlorine substitution products of toluene, 7
Chlorobenzol, 136
Chlorobenzoyl chloride, 310
Chlorobenzenyl trichloride, 310
Chlorodracylic acid, 221
Chloro-isophthalic acid, 481
Chloromeconin, 500
Chlorometatoluic acid, 417
Chlorometaxylenesulphamide, 393
Chloromethylnoropianic acid, 503
α-Chlorometaxylene, 393
Chloromichmic acid, 219
Chloroniceïnic acid, 219
Chloronitrotoluenes, 19
Chloronitrobenzoic acids, 236
Chloroparacresol, 29
Chloroparahydroxybenzaldehyde, 296
Chloroparahydroxybenzoic acid, 334
Chloroparatoluic acid, 420

Chloroparatoluidine, 8
Chlorophthalic acid, 393
α-Chlorophthalic acid, 471
v-Chlorophthalic acid, 471
Chloroparaxylene, 393
Chloropianic acid, 507
Chlororthotoluic acids, 415
α-Chlororthoxylene, 392
v-Chlororthoxylene, 392
Chlorosalicylaldehyde, 292
Chlorosalicylic acid, 313
Chlorosulphobenzoic acids, 274
Chloroterephthalic acid, 488
Chlorotoluene, 7
Chlorotoluic acid, 393
Chlorotoluidines, 68
Choline, 376
Cinnameïn, 90
Cinnamic acid, 90, 135, 297
Cinnamone, 135
Colophonin hydrate, 7
Colophonin, 6
Coniferyl alcohol, 345
Copper benzoate, 161
Copper hippurate, 190
Copper metahydroxybenzoate, 321
Copper parahydroxybenzoate, 328
Copper phthalate, 457
Copper quinate, 384
Copper salicylaldehyde, 287
Copper salicylate, 304
Coumaim, 186
Creosol, 32
Creosote, 32 *et seq.*
α-Cresol, 23
β-Cresol, 23
γ-Cresol 24
Cresolcarboxylic acid, 438
Cresorcinol, 47, 437
Cresorcinolcarboxylic acid, 437
Cresorsellinic acid, 437
Cresotic acid, 423
α-Cresotic acid, 423
β-Cresotic acid, 424
γ-Cresotic acid, 424
Cresyl alcohol, 23
Cresyl benzoate, 164
Cresyl hydrate, 23
Cudbear, 44
Cumaric acid, 297
Cumic acid, 451
Cumino-cyminic acid, 451
Cumol, 386
Cyanobenzylamine, 121
Cyanocarbimidobenzoic acid, 249
Cyanocarboxamidobenzoic acid, 249
Cynanphenin, 199
Cymene, 4
Cymol, 386

D

DIACETORTHO-AMIDOBENZOIC ACID, 239
Diacetotoluquinol, 48
Diamidobenzoic acids, 258
Diamidobenzoic acids, action of nitrous acid on the, 263
α-Diamidobenzoic acid, 258
β-Diamidobenzoic acid, 259
δ-Diamidobenzoic acid, 267
γ-Diamidobenzoic acid, 259
δ Diamidobenzoic acid, 259
δ-Diamidobenzoic acid hydrochloride, 259
δ-Diamidobenzoic acid sulphate, 259
Diamidobenzylsulphonic acid, 109
Diamidocresol, 79
Diamidohydro-acridine ketone, 245
α-Diamidometaxylene, 409
v-Diamidometaxylene, 409
s-Diamidometaxylene, 409
α-Diamidoparaxylene, 410
β-Diamidoparaxylene, 410
γ-Diamidoparaxylene, 410
Diamidosalicylic acid, 318
Diamidoterephthalic acid, 489
α-Diamidotoluene, 72
β-Diamidotoluene, 72
γ-Diamidotoluene, 73
δ-Diamidotoluene, 74
α-Diamidotoluene di-hydrochloride, 7
β-Diamidotoluene hydrochloride, 73
γ-Diamidotoluene hydrochloride, 73
α-Diamidotoluene monohydrochloride 72
α-Diamidotoluene sulphate, 72
β-Diamidotoluene sulphate, 73
γ-Diamidotoluene sulphate, 73
Diamidotoluenes, 72
Diamidotriphenylmethane, 135
Diamines and Triamines of the Xylenes, 409
Dianilidotoluquinone, 49
Dianilidotoluquinone anilide, 49
Dianisbenzhydroxylamine, 342
Dianishydroxamic acid, 340
Diazo-amidobenzene, 18
Diazo-amidotoluene, 74
Diazo-amidotoluic acid, 421
Diazobenzene-amidobenzoic acid, 262
Diazobenzoic acid, 260
Diazobenzoic acid nitrate, 260
Diazobenzoic acid seminitrate, 260
Diazo-derivatives of benzoic acid, 260
Diazo-derivatives of toluene, 74
Diazohemipinic acid, 513
Diazo-imidobenzoic acids, 263
Diazooenzene-amidotoluene, 74
Diazo-salicylic acid, 319
Diazotoluene nitrate, 74
Diazotoluene sulphate, 74
Diazoxybenzoic acid, 267
Dibenzamide, 176
Dibenzamide hydrate, 177
Dibenzanilide, 177
Dibenzanishhydroxylamine, 341
Dibenzarsene iodide, 278
Dibenzarsenic acid, 278
Dibenzarsenious acid, 278

Dibenzenylazoxime, 214
Dibenzenyltriamine, 202
Dibenzhydroxamic acid, 209
Dibenzhydroxylamine, 207
Dibenzidenediamidobenzoic acid, 142
Dibenzidenemetadiamidotoluene, 142
Dibenzidene-orthodiamidotoluene, 142
Dibenzimido-oxide, 197
Dibenzoarsenic acid, 85
Dibenzobenzoximate, 211
Dibenzoylcatechol, 164
Dibenzoylphenylhydrazine, 180
Dibenzoylquinol, 164
Dibenzoylrescorcinol, 164
Dibenzoyl urea, 179
Dibenzenylamidine, 202
Dibenzylamine, 114
Dibenzylamine hydrochloride, 115
Dibenzylamine nitrate, 115
Dibenzylarsenic acid, 126
Dibenzylarsine trichloride, 125
Dibenzylcatechol, 96
Dibenzylcyanimide, 122
Dibenzyl ether, 94
Dibenzylguanidine, 121
Dibenzyloxamide, 121
Dibenzylphosphine, 125
Dibenzylquinol, 96
Dibenzylresorcinol, 96
Dibenzyl sulphone, 107
Dibenzyltolylamine, 118
Dibenzyltoluidine, 118
Dibromanisic acid, 336
Dibromobenzoic acids, 224
Dibromo-gallic acid, 370
Dibromohexhydroterephthalic acid, 486
Dibromolecanoric acid, 434
α-Dibromometaxylene, 394
β-Dibromometaxylene, 394
α-Dibromometaxylenol, 401
Dibromoparacresol, 29
Dibromoparahydroxybenzoic acid, 334
Dibromoparatoluic acid, 420
Dibromoparaxylene, 395
α-Dibromophthalic acid, 472
β-Dibromophthalic acid, 473
Dibromophthalide, 444
Dibromorcinol, 41
Dibromorsellinic acid, 433
Dibromorthoxylene, solid, 394
—— liquid, 394
Dibromoterephthalic acid, 488
Dibromotoluenes, 11
Dibromotetrahydrophthalic acid, 470
Dichloraniaic acid, 336
Dichlorobenzaldehyde, 144
Dichlorobenzenyl trichloride, 196
α-Dichlorobenzoic acid, 221
β-Dichlorobenzoic acid, 222
γ-Dichlorobenzoic acid, 222
δ-Dichlorobenzoic acid, 222
ε-Dichlorobenzoic acid, 222

Dichlorobenzidene chloride, 145
Dichlorobenzoic acids, 221
Dichlorobenzyl alcohol, 100
Dichlorobenzyl chloride, 101
Dichlorohippuric acid, 220
Dichloroparacresol, 29
Dichloroparahydroxybenzoic acid, 334
Dichloroparaxylene, 393
Dichlorophthalic acid, 471
Dichloropiperonal, 348
Dichlororthocresol, 25
Dichlororthoxylene, 393
Dichloro-salicylic acid, 314
Dichlorosilicon orthoditoluide, 87
Dichlorotoluene hexchloride, 10
Dichlorotoluenes, 9
Dichlorotoluquinone, 27, 50
Dicinnyl ketone, 135
Dicyanamidobenzoyl, 241
Diethylbenzamide, 174
Diethylbenzylamine, 116
Diethyl diacetoxyterephthalate, 517
Diethyldiamidoterephthalate, 489
Diethyldibenzylammonium iodide, 117
Diethyl α-hydroxyisophthalate, 495
Diethyl s-hydroxyisophthalate, 495
Diethyl dihydroxyterephthalate, 516
Diethylorthotoluidine, 59
Diethylparadihydroxybenzaldehyde, 349
Di-ethylparatoluidine, 65
Diethylprotocatechuic acid, 355
Diethyl-β-resorcylaldehyde, 349
Diethyl-α-resorcylic acid, 359
Diethyl-β-resorcylic acid, 360
Difluorbenzoic acid, 227
Digallic acid, 371
Dihydro-orthoxylene, 391
Dihydrophthalic acid, 469, 487
Dihydrotoluene, 6
Dihydroxybenzoic acids, 350
Dihydroxybenzyl and Dihydroxy-Benzoyl compounds, 343
Dihydroxyhexhydroterephthalic acid, 487
Dihydroxyisophthalaldehyde, 515
Dihydroxyisophthalic acid, 515
Dihydroxyphthalic acids, 510
Dihydroxyquinone, 520
Dihydroxyterephthalic acid, 515
Dihydroxytoluenes and allied bodies, 31
Dihydroxytolualdehydes, 427
Dihydroxytoluic acids, 428
Dihydroxytoluquinone, 49
Dihydroxy-xylenes, 402
Di-iodoparacresol, 29
Di-iodoparahydroxybenzoic acid, 335
Di-iodosalicylic acid, 315
Dimetatolyl carbamide, 63
Dimetatolyl thiocarbamide, 63
Dimethoxybenzonitril, 361
Dimethoxyorthophthalic acid, 510
Dimethyl acetoxyterephthlate, 496

Dimethylamidophenylhydroxytrichlorethane, 151
Dimethylbenzamide, 174
Dimethylbenzenes, 390
Dimethyldiamidotoluene, 62
Dimethyldihydroxyphthalic acid, 498
Dimethyl α-hydroxyisophthalate, 495
Dimethyl *s*-hydroxyisophthalate, 495
Dimethylhydroxysalicylic acid, 362
Dimethyl hydroxyterephthalate, 496
Dimethylmetamidobenzoic acid, 247
Dimethylmetatoluidine, 61
Dimethylmethylene benzoate, 163
Dimethylnoropianic acid, 503
Dimethylorthotoluidine, 58
Dimethylparadihydroxybenzaldehyde, 349
Dimethylparamidobenzaldehyde, 150
Dimethylparamidobenzoic acid, 253
Dimethylparatoluidine, 65
Dimethylparatolyl phosphine, 84
Dimethyltolylphosphine oxide, 84
Dimethylphenylenebenzenylamide ammonium iodide, 205
Dimethylphosphine-oxide benzoic acid, 277
Dimethylprotocatechuic acid, 354
Dimethylprotocatechuicaldehyde, 346
Dimethyl-β-resorcylaldehyde, 349
Dimethyl-α-resorcylic acid, 358
Dimethyl-β-resorcylic acid, 360
Dimethyl-γ-resorcylic acid, 361
Dinitro-amidobenzoic acids, 257
Dinitro-anisic acid, 337
Dinitro-anthranilic acid, 257
α-Dinitrobenzoic acid, 234
β-Dinitrobenzoic acid, 234
γ-Dinitrobenzoic acid, 234
δ-Dinitrobenzoic acid, 235
ε-Dinitrobenzoic acid, 235
Dinitrobenzoic acids, 234
Dinitrobenzysulphonic acid, 109
Dinitro-diphenylamine-orthocarboxylic acid, 245
Dinitro-*v*-hydroxyphthalic acid, 493
Dinitrohydroxyterephthalic acid, 496
s-Dinitrometaxylene, 396
v-Dinitrometaxylene, 396
α-Dinitro-orcinol, 41
β-Dinitro-orcinol, 42
Dinitro-orthamidobenzoic acid, 257
Dinitro-orthocresol, 26
α-Dinitro-orthotoluidine, 71
Dinitro-orthoxylene, 396
Dinitroparacresol, 30
Dinitroparahydroxybenzoic acid, 335
Dinitroparamidobenzoic acid, 258
Dinitroparaxylidine, 408
α-Dinitroparaxylene, 397
β-Dinitroparaxylene, 397
γ-Dinitroparaxylene, 397
Dinitrophthalic acid, 475
Dinitrosalicylic acid, 317
γ-Dinitrotoluene, 17
Dinitrotoluene, ordinary, 16; symmetric, 17
Dinitrotoluenes, 16
Dinitrotoluidine, 18
β-Dinitrotoluidine, 71
γ-Dinitrotoluidine, 71
Dinitrotoluidines, 71
γ-Dinitrotolylphenylamine, 18
Diorsellinic acid, 433
Di-orthotolylamine, 59
Di-orthotolylcarbamide, 59
Di-orthotolyl thiocarbamide, 60
Diparahydroxybenzoylparahydroxybenzoic acid, 331
Diparatolylamine, 66
Diparatolylarsenic acid, 85
Diparatolyl carbamide, 66
Diparatolylhydrazine, 75
Diparatolylnitrosamine, 66
Diparatolyl thiocarbamide, 67
Diphenylbenzene, 452
Diphenylbenzenylamidine, 204
Diphenylorthoxylylenediamine, 440
Diphenylparamidobenzenylamidine, 204
Diphenylphthalamic acid, 465
Diphenylphthaleïn, 465
Diphenylthiobenzamide, 178
Diphthalyl, 458, 460
Disalicylamide, 312
Disalicylic acid, 308
α-Disulphobenzoic acid, 274
β-Disulphobenzoic acid, 274
Disulphobenzoic acids, 274
Disulphometahydroxybenzoic acid, 326
Disulphorthotoluic acid, 416
Dithiobenzoic acid, 172
Dithiometahydroxybenzoic acid, 325
Dixylylamine, 412
Dragonic acid, 329
Drupaceæ, 131

E.

ERYTHRELINIC ACID, 429
Erythric acid, 429
Erythrinbitter, 428
Erythrylin, 428
Erythrin, 428, 431, 434
β-Erythrin, 435
Erythroglucin, 430
Ethereal salts of Benzyl, 96
Ethereal salts of salicylic acid, 306
Ethereal salts of salicylic ethers, 307
Ethers of benzoic acid, 160
Ethers of benzyl with the dihydroxybenzenes, 95
Ethers of phthalic acid, 457
Ethidenedibenzamide, 176
Ethoxycarbimidamidobenzoic acid, 250
Ethoxycyanamidobenzoyl, 242
Ethoxymethoxybenzonitril, 361
Ethoxynitrobenzonitril, 361
Ethyl amido-isophthalate, 482

Ethyl α-amidophthalate, 476
Ethyl v-amidophthalate, 475
Ethyl anisbenzhydroxamate, 340
Ethyl anishydroxamate, 339
Ethylanishydroxamic acid, 339
α-Ethylbenzanishydroxamate, 340
β-Ethylbenzanishydroxamate, 340
Ethyl benzenylamidoximecarboxylate, 214
Ethenylbenzenylazoxime, 214
α-Ethylbenzhydroxamic acid, 211
Ethyl benzhydroxamate, 209
Ethyl benzoate, 161
Ethyl benzoyl-glycollate, 165
Ethyl benzoyl-lactate, 165
Ethylbenzoyl thio-urea, 179
Ethyl-benzylamidine, 202
Ethylbromosalicylaldehyde, 292
Ethylene benzoate, 162
Ethyl-β-diamidotoluene, 73
α-Ethyl dibenzhydroxamate, 210
β-Ethyl dibenzhydroxamate, 210
Ethyl dibenzylamine, 117
Ethyl dibromoterephthalate, 488
Ethyl dihydroxyquinoneterephthalate, 519
Ethylenebenzamide, 174
Ethyleneprotocatechuic acid, 356
Ethylene salicylate, 306
Ethylene salicylic acid, 306
Ethyl ether of benzenylamidoxime, 213
Ethyl ethylenesalicylate, 307
Ethyl ethylsalicylate, 307
Ethyl gallate, 369
Ethyl hemipinimide, 514
Ethyl hippurate, 190
β-Ethylhydroxamic acid, 211
Ethyl hydroxysalicylate, 362
Ethyl isophthalate, 479
Ethyl metacyanobenzoate, 480
Ethyl meta-ethoxybenzoate, 322
Ethyl metahydroxybenzoate, 321
Ethyl metanitrobenzoate, 231
Ethyl metasulphamidobenzoate, 272
Ethyl metasulphobenzoic acid, 271
Ethyl metatoluate, 417
Ethyl methylsalicylate, 307
Ethyl nitro-isophthalate, 482
Ethylnitrolic acid, 468
Ethyl opianate, 505
Ethyl orsellinate, 433
Ethyl orthobenzoate, 194
Ethyl orthocyanobenzoate, 468
Ethyl orthonitrobenzoate, 230
Ethyl orthotoluate, 414
Ethylorthotoluidine, 59
Ethyl paracyanobenzoate, 485
Ethylparadihydroxybenzaldehyde, 349
Ethyl para-ethoxybenzoate, 330
Ethyl parahydroxybenzoate, 330
Ethyl paramethoxybenzoate, 330
Ethyl paranitrobenzoate, 232
Ethyl paratoluate, 419
Ethylparatoluidine, 65
Ethyl phthalate, 457
Ethyl phthalimide, 464
Ethylphthalylhydroxylamine, 467
Ethyl piperonate, 356
Ethyl pyro-gallolcarboxylate, 379
Ethyl quinate, 385
Ethyl α-resorcylate, 358
Ethyl salicylaldehyde, 287
Ethyl salicylate, 306
Ethyl terephthalate, 484
Ethyl tetracetylquinate, 385
Ethyl tetrachlorophthalate, 472
Ethyl tetrahydroxyterephthalate, 520
Ethyl thiobenzoate, 171
Ethyltolyl carbamate, 67
Ethylvanillic acid, 355
Ethyl veratrate, 355
Ethysalicylic acid, 306
Evernic acid, 435
Everninic acid, 435

F.

Ferric benzoate, 161
Fluorine substitution products of toluene, 13
Formortho-amidobenzoic acid, 239
Fluotoluene, 13

G.

Gallamide, 370
Gallates, the, 368
Gallic acid, 363, 381
Gallocarboxylic acid, 519
Gallocyanin, 377
Gentisic acid, 362
Gentisinaldehyde, 349
Glucovanillic acid, 352
Glucovanillin, 347
Glucovanillyl alcohol, 347
Guanidodibenzoic acid, 250

H.

Halogen compounds of benzoyl, 168
Halogen substitution products, 118
Halogen substitution products of benzoic acid, 216
Halogen substitution products of phthalic acid, 471
Halogen substitution products of the Toluidines, 67
Halogen substitution products of the Xylenes, 392
Helicin, 288
Helicoïdin, 289
Hemipinic acid, 497, 510
Hemipinic anhydride, 511
Hemipinimide, 513
Hemipinimidine, 501

Heptacarbure quadrihydrique, 3
Hexbromobenzene, 12
Hexchloroxylone, 34
Hexhydrometaxylene, 391
Hexhydroparaxylene, 392
Hexhydrophthalic acid, 470
Hexhydroterephthalic acid, 486
Hexhydrotoluene, 7
Hexmethyl-δ-diamidobenzoic acid, 259
Hexnitrodiparatolylamine, 66
Hipparin, 175
Hippuramide, 191
Hippuramido-acetic acid, 191
Hippurates, the, 189
Hippurglycollamide, 192
Hippuric acid, 181, 383 ; properties, 188
Homocatechol, 31
Homocatechol dimethyl ether, 32
Homocatechol monomethyl ether, 32
Homo-erythrin, 435
Homohydroxysalicylic acid, 438
Homopyrocatechin, 31
Homorcinol, 402
Homosalicylic acids, 423
Homosaligenin, 422
Hydrazenebenzoic acids, 264
Hydrazine-derivatives of Toluene, 75
Hydrazobenzoic acids, 265
α-Hydrazotoluidine, 79
β-Hydrazotoluidine, 79
Hydrobenzamide, 139, 140
Hydrobenzamide trialdehyde, 449
Hydrobenzamidetricarboxylic acid, 449
Hydrobenzoic acid, 159
Hydrobenzuric acid, 192
Hydrobenzyluric acid, 192
Hydrophlorone, 403
Hydrophthalide, 444
Hydrosalicylamide, 291
Hydroxybenzaldehydes, 285
Hydroxybenzidene-amidobenzoic acid, 291
Hydroxybenzoic acids, 297
Hydroxybenzyl alcohols, 279
Hydroxybenzyl group, 279
Hydroxybenzyluric acid, 192
α-Hydroxyisophthalic acid, 494
s-Hydroxyisophthalic acid, 495
v-Hydroxyisophthalic acid, 495
Hydroxyisophthalic acid, 303
Hydroxylamine derivatives containing three acid radicals, 341
Hydroxymetaxyloquinone, 404
Hydroxymethylbenzoic acids, 442
Hydroxymethyldihydroxybenzoic acids, 497
Hydroxymethyldimethoxybenzoic acid, 500
Hydroxymethylhydroxybenzoic acid, 490
v-Hydroxyorthophthalic acid, 493
Hydroxyphthalamic acid, 467
α-Hydroxyphthalic acid, 492
Hydroxyphthalic acids, 492
α-Hydroxyphthalic anhydride, 493
Hydroxyquinolcarboxylic acid, 380, 381
Hydroxysalicylic acid, 361
Hydroxyterephthalic acid, 495
Hydroxytolualdehydes, 422
s-Hydroxytoluic acid, 425
Hydroxytoluic acids, 423
Hydroxytoluquinonoxime, 52
Hydroxytrinesic acid, 303, 494
Hydroxy-xylenes, 399
Hypogallic acid, 498

I.

Imide of metadiazobenzoic acid, 264
Insolinic acid, 451
Iodamidobenzoic acids, 255
Iodanisic acid, 337
Iodine substitution products, 41
Iodine substitution products of Toluene, 13
Iodo-isophthalic acid, 481
Iodomeconin, 500
Iodometahydroxybenzoic acid, 323
Iodonitrobenzoic acids, 237
Iodoparacresol, 29
Iodoparahydroxybenzaldehyde, 296
Iodoparahydroxybenzoic acid, 335
Iodoparatoluic acid, 420
Iodosalicylic acid, 314
Iodotoluenedisulphonic acid, 22
Iodotoluidines, 68
Iron gallate, 369
Isobutyl hippurate, 191
Isobutyl terephthalate, 484
Isodiazoxybenzoic acid, 267
Isohemipinic acid, 515
Isonitrosobenzyl ether, 98
Isonoropianic acid, 508
Isophthalalcohol, 440
Isophthalaldehyde, 447
Isophthalic acid, 451, 479
Isophthalic acid, addition products of, 481
Isophthalic acid, substitution products of, 481
Isophthalamide, 480
Isophthalonitril, 481
Isophthalyl chloride, 480
Isopianic acid, 509
Isopropyl benzoate, 162
Isopropylsalicylic acid, 306
Isopropyl terephthalate, 484
Isorcinol, 47
Isosulphometahydroxybenzoic acid, 325
Isotrichloroglyceric acid, 368
Isovanillic acid, 353
Isovanillin, 346
Isoxylol, 387

J.

JUGLONIC acid, 493

K.

KINOÏN, 374
Kino-red, 374

L.

LEAD benzoate, 161
Lead benzyl mercaptide, 106
Lead benzylsulphonate, 108
Lead dithiobenzoate, 172
Lead gallate, 369
Lead hippurate, 190
Lead opianate, 504
Lead opianylsulphite, 507
Lead parahydroxybenzoate, 328
Lead phthalate, 457
Lead proto-catechuate, 352
Lead quinate, 384
Lead salicylaldehyde, 287
Lead salicylate, 304
Lecanoric acid, 429, 432, 433
Lecanorin, 429
Lithium salicylate, 303
Litmus, 45
Luteolin, 357

M.

MACLURIN, 356
Magnesium hippurate, 189
Maluchite-green, 135
Mandelic acid, 131
Meconin, 497, 500
ψ-Meconin, 501
Meconinic acid, 500
Meconiosin, 502
Menyanthin, 423
Menyanthol, 423
Mercuric benzamide, 174
Mercuric benzoate, 161
Mercury benzyl mercaptide, 105
Mercury derivatives of Toluene, 87
Mercury orthotolyl, 88
Mercury paratolyl, 88
Meta-acetobenzyl acetate, 283
Meta-acetoxybenzoic acid, 322
Meta-azotoluene, 76
Meta-benzamoxalic acid, 248, 249
Metabenzenyltrichlorophosphoryl chloride, 322
Metabenzobetaïne, 248
α-Metabenzo-creatine, 252
β-Metabenzo-creatine, 252
Metabenzoglycocyamine, 251
Metabenzosarcosine, 247
Metabromobenzaldehyde, 145
Metabromobenzoic acid, 223
Metabromobenzyl bromide, 102
Metabromotoluene, 11
Metacarbamidobenzoic acid, 251
Metacarbonylphenylphosphoryl chloride, 322
Metacarboxyorthophosphoric acid, 322
Metachlorobenzaldehyde, 144
Metachlorobenzoic acid, 219
Metachlorobenzonitril, 220
Metachlorobenzoyl chloride, 220, 383
Metachlorohippuric acid, 220
Metachlorotoluene, 8
Metacresol, 24, 27
Metacresyl benzoate, 164
Metacresyl oxide, 27
Metacyanobenzoic acid, 480
Metadiamidobenzylamine, 120
Metadiazo-amidobenzoic acid, 262
Metadiazobenzamide nitrate, 261
Metadiazobenzoic acid, 261
Metadiazobenzoic acid imide, 264
Metadiazobenzoic acid nitrate, 261
Metadiazobenzoic acid perbromide, 261
Metadiazobenzoic acid platinichloride, 261
Metadiazobenzoic acid sulphate, 261
Metadiazobenzonitril nitrate, 262
Metadihydroxybenzaldehyde, 348
Metadinitrobenzylamine, 119
Metadithiobenzoic acid, 272
Metaditolylamine, 62
Meta-ethoxybenzoic acid, 322
Metafluorbenzoic acid, 226
Metafluorhippuric acid, 226
Metaguanidobenzoic acid, 251
Metahomometahydroxybenzoic acid, 425
Metahomomethoxycalicylaldehyde, acid, 428
Metahomoparahydroxybenzaldehyde, 422
Metahomoparahydroxybenzoic acid, 426
Metahomosalicylaldehyde, 422
α-Metahomosalicylic acid, 424
β-Metahomosalicylic acid, 424
Metahydrazinebenzoic acid, 264
Metahydrazobenzoic acid, 266
Metahydrazotoluene, 76
Metahydroxybenzaldehyde, 293
Metahydroxybenzamide, 323
Metahydroxybenzanilide, 323
Metahydroxybenzenylamidoxime, 216
Metahydroxybenzoates, 320
Metahydroxybenzoic acid, substitution products of, 323
Metahydroxybenzonitril, 323
Metahydroxybenzoic acid, 320
Metahydroxybenzoylsulphuric acid, 326
Metahydroxybenzuric acid, 323
Metahydroxybenzyl acetate, 283
Metahydroxybenzyl alcohol, 283

Metahydroxybenzyl diacetate, 283
Metahydroxyorthotoluic acid, 425
Metahydroxyparatoluic acid, 426
Meta-iodobenzoic acid, 225
Meta-iodotoluene, 13
Metamethoxybenzoic acid, 321
Metamethoxysalicylaldehyde, 349
β-Metamethoxysalicylaldehyde, 348
Metamidobenzaldoxime, 150
Metamidobenzaldehyde, 150
Metamidobenzamide, 247
Metamidobenzenylamidoxime, 216
Metamidobenzoic acid, 246, 248, 252
Metamidobenzoic acid hydrochloride, 247
Metamidobenzonitril, 247
Metamidobenzylphenylamine, 120
Metamidoparamethyltoluidine, 73
Metamidoparazotoluene, 78
Metanitrobenzaldehyde, 147
Metanitrobenzaldoxime, 147
Metanitrobenzamide, 231
Metanitrobenzenylamidoxime, 216
Metanitrobenzidene bromide, 147
Metanitrobenzidene chloride, 147
Metanitrobenzoic, 230
Metanitrobenzoic acid, 228
Metanitrobenzonitril, 232
Metanitrobenzoyl chloride, 231
Metanitrobenzyl alcohol, 104
Metanitrobenzylamine, 119
Metanitrobenzylamines, 119
Metanitrobenzyl chloride, 104
Metanitrobenzylphenylamine, 119
Metanitrohippuric acid, 232
Metanitromethylmetahydroxybenzaldehyde, 294
Metanitro-orthotoluidine, 69
Metanitropara-ethyltoluidine, 71
Metanitroparamethyltoluidine, 71
Metanitroparatoluidine, 70
Metanitrotoluene, 16
Metaphlorone, 404
Metaphthalic acid 479
Metasulphamidobenzoic acid, 272
Metasulphamido-orthotoluic acid, 416
Metasulphobenzamide, 271
Metasulphobenzoates, 270
Metasulphobenzoic acid, 269
Metasulphobenzoyl chloride, 271
Metathiocresol, 31
Metathiohydrobenzoic acid, 272
Metatolualdehyde, 413
Metatoluic acid, 416
Metatoluidine, 60
Metatoluidine hydrochloride, 61
Metatoluidine nitrate, 61
Metatoluidine sulphate, 61
Metatolunitril, 417
Metatoluyl chloride, 417
Metatoluylenediamine, 72
Metatolyl carbamide, 63
Metatolyl mustard oil, 63
Metatolylstibine, 86
Metatolyl thiocarbamide, 63
Metatriamidobenzylamine, 120
Metatrinitrobenzylamine, 119
Meta-uramidobenzoic acid, 250
Meta-urethanebenzoic acid, 251
Metaxylene, 388, 389, 391
a-Metaxylenesulphamide, 399
a-Metaxylenesulphonic acid, 398
v-Metaxylenesulphonic acid, 399
a-Metaxylenesulphonic chloride, 398
a-Metaxylenol, 400
s-Metaxylenol, 401
v-Metaxylenol, 401
a-Metaxylenyl acetate, 401
Metaxylidenehydrazine, 413
Metaxylidene tetrachloride, 447
Metaxylylene alcohol, 440
Metaxylylene bromide, 441
Metaxylylene chloride, 441
Metaxylylene ethyl ether, 440
a-Metaxylenyl methyl ether, 400
a-Metaxylidine, 406
s-Metaxylidine, 407
v-Metaxylidine, 406
Metazobenzoic acid, 266
Metazoxybenzoic acid, 266
Methenylamidorthocresol, 26
Metaxyloquinol, 403
Metaxyloquinone, 404
Metaxylorcinol, 402
Metaxylyl acetate, 412
Metaxylyl alcohol, 411
Metaxylyl bromide, 412
Metaxylyl chloride, 412
Metaxylyl ethyl ether, 411
a-Methoxyisophthalic acid, 494
v-Methoxyisophthalic acid, 495
Methoxynitrobenzonitril, 361
Methoxyterephthalic acid, 496
Methyl aldehydovanillate, 509
Methyl amido-anisate, 338
Methylamido-anisic acid, 338
Methyl amido-isophthalate, 482
Methyl amido-terephthalate, 489
Methylbenzene, 3
Methyl benzoate, 161
Methylbenzoylphenylhydrazine, 180
Methylbenzyl, 387
Methyl benzylsalicylate, 307
Methylbromosalicylaldehyde, 292
Methyl bromoterephthalate, 488
Methyl chloroterephthalate, 488
Methylcinnyl ketone, 135
Methyl cresolcarboxylate, 439
Methyl-β-diamidotoluene, 73
Methyldibenzoylphenylhydrazine, 180
Methyl dimethylamidosalicylate, 318
Methylenedibenzamide, 175
Methyleneprotocatechuicaldehyde, 347
Methyl ethylsalicylate, 307
Methyl hippurate, 190
a-Methylhydroquinoneformic acid, 362
a-Methylhydroxyphthalic acid, 493
v-Methylhydroxyphthalic acid, 493

Methylhydroxysalicylic acid, 362
Methylhypogallic acid, 498
Methyl iodide, 36
Methyl isocyanate, 518
Methylisonoropianic acid, 508
Methylisophthalate, 479
Methyl isopropylsalicylate, 307
Methylmetahomoparahydroxybenzoic acid, 427
α-Methylmetahomosalicylic acid, 424
Methylmetahydroxybenzaldehyde, 293
Methylmetamidobenzoic acid, 247
Methylmetatoluidine, 61
Methyl nitrite, 578
Methyl-nitro-isophthalate, 482
Methylnitrosalicylaldehyde, 292
Methyl nitroterephthalate, 489
Methylnorhemipinic acid, 514
Methylnormeconin, 498, 501
Methylnoropianic acid, 498, 502
Methyl opianate, 505
Methyl orsellinate, 432
β-Methylorthodihydroxybenzaldehyde, 348
α-Methylorthobenzoglycocyamidine, 243
β-Methylorthohomometahydroxybenzoic acid, 426
Methylorthohomoparahydroxybenzoic acid, 427
Methylorthohomosalicylic acid, 424
Methylorthotoluidine, 58
Methylorthotolylnitrosamine, 58
Methylparadihydroxybenzaldehyde, 349
Methylparahomosalicylic acid, 424
Methylparahydroxybenzaldehyde, 295
Methylparahydroxybenzoate, 295, 328
Methylparahydroxybenzoyl chloride, 332
Methyl paramethoxybenzoate, 330
Methyl paratoluate, 419
Methylparatoluidine, 64
Methylphthalate, 457
Methylphthalimidine, 445
Methylprotocatechuate, 352
Methylpyrogallic acid, 53
Methylpyrogallol, 53
Methylpyrogallol dimethyl ether, 54
Methyl salicylaldehyde, 287
Methyl salicylate, 305
Methyl salicylic acid, 305
Methyl terephthalate, 484
Methyl tetrahydroterephthalate, 486
Methyltoluol, 387
Methyl vanillate, 352
Methylvanillin, 346
Methyl veratrate, 354
Monamidobenzoic acids, 237
Monethyl dihydroxyterephthalate, 517
Monobromobenzoic acids, 223
Monobromoparaxylenol, 401
Monobromophthalide, 443
Monobromorcinol, 41
Monobromotoluenes, 10
Monochlorobenzoic acids, 217
Monochlorobenzenyl trichloride, 196
Monochlorotoluenes, 8
Monofluorbenzoic acids, 226
Monohydroxytoluenes and allied bodies, 23
Mono-iodobenzoic acids, 225
Mono-iodorcinol, 41
Mononitrobenzoic acids, 229
Mononitrotoluenes, 13
Monosulphobenzoic acids, 268
Monoxylylamine, 412
Morintannic acid, 356

N.

NAPHTHALAMIDE, 463
Naphthalic acid, 450
Naphthesic acid, 450
Nitradiazobenzoic acid, 262
Nitranilic acid, 520
ε-Nitro-amidobenzamide, 257
α-Nitro-amidobenzoic acid, 256
β-Nitro-amidobenzoic acid, 256
γ-Nitro-amidobenzoic acid, 256
δ-Nitro-amidobenzoic acid, 256
ε-Nitro-amidobenzoic acid, 257
ζ-Nitro-amidobenzoic acid, 257
η-Nitro-amidobenzoic acid, 257
Nitro-amidobenzoic acids, 255
Nitro-amidosalicylic acid, 318
Nitro-anisic acid, 33
Nitrobenzinic acid, 227
Nitrobenzoene, 4
Nitrobenzoic acids, 233
Nitrobenzylsulphonic acid, 109
Nitrococcusic acid, 425
Nitro-diamidometaxylene, 409
Nitro-dimethylmetatoluidine, 62
Nitro-dracyl, 4
Nitro-dracylic acid, 228
Nitrogen bases of benzyl, 110
Nitrogen compounds of benzoyl, 172
Nitrohemipinic acid, 511
Nitro-isophthalic acid, 482
Nitromeconin, 500
Nitro-ψ-meconin, 501
Nitrometacresol, 27
α-Nitrometahydroxybenzaldehyde, 293
β-Nitrometahydroxybenzaldehyde, 293
γ-Nitrometahydroxybenzaldehyde, 293
Nitrometahydroxybenzoic acids, 323
α-Nitrometahydroxybenzoic acid, 324
β-Nitrometahydroxybenzoic acid, 324
γ-Nitrometahydroxybenzoic acid, 324
η-Nitrometahydroxybenzoic acid, 324
Nitrometatoluic acids, 417
α-Nitrometaxylene, 396
s-Nitrometaxylene, 396
ν-Nitrometaxylene, 396
α-Nitro α-metaxylidine, 408
s-Nitro-s-metaxylidine, 408
ν-Nitrol-α-metaxylidine, 408

α-Nitro-s-metaxylidine, 408
Nitromethane, 518
Nitromethylnoropianylhydrazide, 508
Nitromethylnoropianic acid, 503
Nitromethylnorhemipinic acid, 514
Nitro-opianic acid, 507
Nitro-opianylphenylhydrazide, 508
α-Nitro-orcinol, 41
β-Nitro-orcinol, 41
α-Nitro-orthocresol, 25
β-Nitro-orthocresol, 26, 51
γ-Nitro-orthocresol, 26
Nitro-orthotoluic acids, 415
α-Nitro-orthoxylene, 395
ν-Nitro-orthoxylene, 395
α-Nitroparacresol, 30
β-Nitroparacresol, 30
Nitroparahydroxybenzoic acid, 335
Nitroparahydroxybenzaldehyde, 296
α-Nitroparatoluic acid, 421
β-Nitroparatoluic acid, 421
β-Nitroparatolunitril, 421
Nitroparaxylene, 397
α-Nitroparaxylidine, 408
β-Nitroparaxylidine, 408
γ-Nitroparaxylidine, 408
α-Nitrophthalic acid, 474
ν-Nitrophthalic acid, 473
Nitrophthalic acids, 473
α-Nitrophthalicanhydride, 475
α-Nitro-salicylaldehyde, 292
β-Nitrosalicylaldehyde, 292
Nitrosalicylic acids, 315
α-Nitrosalicylic acid, 315
β-Nitrosalicylic acid, 316
Nitrosodibenzylamine, 116
Nitroso-dimethylmetatoluidine, 62
Nitrosohemipinimidine, 501
Nitrosomethylmetanitrobenzene, 147
Nitrosomethylnitrobenzene, 147
Nitrosomethylparatoluidine, 65
Nitrosometracresol, 51
Nitrosoparaxylorcinol, 402
Nitrosophthalimidine, 444
Nitro-substitution products, 41, 293
Nitro-substitution products of benzoic acid, 227
Nitro-substitution products of toluene, 13
Nitro-substitution products of the xylenes, 395
Nitrosulphobenzoic acids, 275
Nitroterephthalamide, 489
Nitro-terephthalaldehyde, 449
Nitroterephthalaldehydic acid, 449
Nitro-terephthalic acid, 488
Nitrotoluene, 13
β-Nitrotoluene, 15
Nitrotoluidine, 15
Nitrotoluidines, 69
Nitro-uramidobenzoyl, 242
Nitroxylidines, 408
Norhemipinic acid, 498
Normal barium hydroxamate, 208
Normal barium metasulphobenzoate, 270
Normal barium α-nitrosalicylate, 316
Normal barium β-nitrosalicylate, 316
Normal barium parasulphobenzoate, 273
Normal barium phthalate, 457
Normal calcium benzamoxalate, 245
Normal ethyl metasulphobenzoate, 270
Normal ethyl α-nitrophthalate, 475
Normal ethyl ν-nitrophthalate, 474
Normal lead metasulphobenzoate, 270
Normal methyl sulphinidephthalate, 478
Normal potassium hemipinate, 510
Normal potassium metasulphobenzoate, 270
Normal potassium sulphinidephthalate, 477
Normal silver hemipinate, 510
Normal silver sulphinidephthalate, 477
Normal sodium dihydroxyterephthalate, 516
Normeconin, 498
Noropianic acid, 498, 502

O.

Octyl benzoate, 162
Octacetylhelicoidin, 289
Oil of bitter almonds, 132
Opianic acid, 497, 503
Opianic anhydride, 505
Opianoxime anhydride, 513
Opianyl, 497
Opianylphenylhydrazide, 507
Opianyl sulphurous acid, 506
Opinic acid, 514
Orceïn, 44
α-Orceïn, 44
β-Orceïn, 44
Orcin, 37
β-Orcin, 402
Orcinol, 37, 429 ; properties, 39
Orcinol acetate, 40
Orcinolazobenzene, 40
Orcinol diethylcarbonate, 40
Orcinol dimethyl ether, 40
Orcinol monomethyl ether, 40
Orcinol, substitution products of, 41
Orcylaldehyde, 427
Ornithine, 193
Ornithuric acid, 192, 193
α-Orsellic acid, 429
Orsellinic acid, 432, 438
α-Orsellinic acid, 429
Orthamidobenzaldoxime, 149
Orthamidobenzaldehyde, 149
Orthamidobenzyl alcohol, 105
Ortho-aldehydometahydroxybenzoic acid, 492
Ortho-aldehydoparahydroxybenzoic acid, 491

Ortho-aldehydophenoxyacetic acid, 289
Ortho-aldehydosalicylic acid, 491
Ortho-amidobenzamide, 240
Ortho-amidobenzoic acid, 237
Ortho-amidobenzoic acid, hydrochloride, 239
Ortho-amidobenzonitril, 240
Ortho-amidopara-azotoluene, 78
Ortho-azobenzoic acid, 265
Ortho-azotoluene, 75
Ortho-azoxybenzoic acid, 265
Ortho-azoxytoluene, 77
Orthobenzamoxalic acid, 244
Orthobenzidenephenylhydrazine, 291
α-Orthobenzocreatinine, 243
β-Orthobenzocreatinine, 244
Orthobenzoglycocyamidine, 243
Orthobenzoic acid, 194
Orthobenzoylhydrazide, 264
Orthobenzyl thioformate, 106
Orthobromobenzaldehyde, 145
Orthobromobenzoic acid, 223
Orthobromobenzyl alcohol, 102
Orthobromo-benzylamine, 118
Orthobromobenzyl bromide, 102
Orthobromotoluene, 10
Orthocarbonylphenylphosphoryl chloride, 311
Orthocarboxylphenylphosphoric acid, 311
Orthochlorobenzaldehyde, 143
Orthochlorobenzidene chloride, 143
Orthochlorobenzoic acid, 144, 217
Orthochlorobenzonitril, 218
Orthochlorobenzoyl chloride, 218, 462
Orthochlorocarbonylphenyl metaphosphate, 311
Orthochloroparanitrotoluene, 19
Orthochlorotoluene, 8
Orthocresol, 24, 25
Orthocresyl benzoate, 164
Orthocresyl oxide, 25
Orthocyanobenzoic acid, 468
Orthodiazobenzoic acid nitrate, 261
Orthodiazobenzoic acid seminitrate, 261
Orthodibromo-benzylamine, 119
α-Orthodihydroxybenzaldehyde, 343
Orthodihydroxybenzoic acid, 350
Orthodinitrotoluene, 17
Orthofluorbenzoic acid, 226
Orthofluorhippuric acid, 226
α-Orthohomometahydroxybenzoic acid, 426
β-Orthohomometahydroxybenzoic acid, 426
Orthohomoparahydroxybenzaldehyde, 422
Orthohomoparahydroxybenzoic acid, 427
Orthohomosalicylaldehyde, 422
Orthohomosalicylic acid, 424
Orthohydrazinebenzoic acid, 264
Orthohydrazobenzoic acid, 265
Orthohydroazotoluene, 75
Orthohydroxybenzaldehyde, 285
Orthohydroxybenzidene acetate, 290
Orthohydroxybenzidene compounds, 290
Orthohydroxybenzidenoxime, 290
Orthohydroxybenzoic acid, 297
Orthohydroxybenzyl alcohol, 279
Orthohydroxybenzyl ethyl ether, 280
Orthohydroxybenzyl glucoside, 281
Orthohydroxybenzyl methyl ether, 280
Orthohydroxymetatolualdehyde, 422
α-Orthohydroxymetatoluic acid, 423
Orthohydroxymetaxylyl alcohol, 422
Orthohydroxymethylbenzoic acid, 442
Orthohydroxymethylparahydroxybenzoic acid, 490
Orthohydroxymethylsalicylic acid, 490
Orthohydroxyparatolualdehyde, 422
Orthohydroxyparatoluic acid, 424
Orthohydroxymetatolualdehyde, 422
ν-Orthohydroxymetatoluic acid, 424
Ortho-iodobenzoic acid, 225
Ortho-iodotoluene, 13
Orthomethoxybenzyl alcohol, 280
Orthomethoxyparahydroxybenzaldehyde, 348
Orthomethyl-β-resorcylic acid, 360
Orthonitrobenzoyl chloride, 230
Orthonitrobenzyl alcohol, 104
Orthonitrobenzaldehyde, 146, 240
Orthonitrobenzaldoxime, 146
Orthonitrobenzoic acid, 228, 229
Orthonitrobenzonitril, 230
Orthonitrobenzyl chloride, 105
Orthonitrobenzyl iodide, 105
Orthonitrometatolualdehyde, 413
α-Orthonitrometatoluidine, 70
β-Orthonitrometatoluidine, 70
α-Orthonitromethylmetahydroxybenzaldehyde, 294
β-Orthonitromethylmetahydroxybenzaldehyde, 294
α-Orthonitro-orthotoluidine, 69
β-Orthonitro-orthotoluidine, 69
Orthonitroparatoluidine, 70
Orthonitrophthalide, 446
Orthonitrotoluene, 15
Orthosulphamidobenzoic acid, 268
Orthosulphobenzoic acid, 268
Orthothiocresol, 31
Orthotolualdehyde, 413
Orthotoluamide, 414
Orthotoluic acid, 414
Orthotoluidine, 57
Orthotoluidine hydrobromide, 58
Orthotoluidine hydrochloride, 58
Orthotoluidine nitrate, 58
Orthotoluidine oxalate, 58
Orthotoluidine sulphate, 58
Orthotolunitril, 414
Orthotoluyl chloride, 414

Orthotoluylarsenic acid, 86
Orthotoluylenediamine, 72
Orthotolyl carbamide, 59
Orthotolyl isocyanate, 59
Orthotolyl mustard oil, 60
Orthotolylphosphenilic acid, 84
Orthotolylphosphenylous acid, 84
Orthotolylphosphorus dichloride, 84
Orthotolylstibine, 86
Orthotolyl thiocarbamide, 59
Orthotribromo-benzylamine, 119
Ortho-uramidobenzoic acid, 243
Orthoxylene, 388, 389, 390
α-Orthoxylenol, 400, 401
υ-Orthoxylenol, 400
Orthoxylenesulphonamide, 398
Orthoxylenesulphonic acid, 398
Orthoxylenesulphonic chloride, 398
Orthoxylidene tetrachloride, 447
α-Orthoxylidine, 406
υ-Orthoxylidine, 406
Orthoxyloquinol, 403
Orthoxyloquinone, 404
Orthoxylyl alcohol, 411
Orthoxylyl bromide, 412
Orthoxylyl chloride, 412
Orthoxylylene acetate, 440
Orthoxylylene alcohol, 439
Orthoxylylene bromide, 440
Orthoxylylene chloride, 439
Orthoxylylene ethyl ether, 439
Orthoxylylene iodide, 440
Orthoxylylene sulphide, 440
Orthrin, 128
Orthylene, 439
Oxalamidobenzoic acid, 249
Oxalanthranilic acid, 244
Oxides of benzoyl, 166
Oxybenzonitrisulphuric acid, 199
Oxybenzuramic acid, 250

P.

PARA-ACETOBENZYL ACETATE, 284
Para-acetoxybenzoic acid, 330
Para-aldehydometahydroxybenzoic acid, 492
Para-aldehydosalicylic acid, 491
Para-amidohydroxymethylbenzoic acid, 446
Para-amidopara-azotoluene, 78
Para-azotoluene, 76
Parabenzidene sulphide, 138
Parabenzophosphenilic acid, 84
Parabromobenzaldehyde, 145
Parabromobenzoic acid, 224
Parabromobenzyl acetate, 102
Parabromobenzyl alcohol, 101
Parabromobenzyl bromide, 101
Parabromotoluene, 11
Paracarbamidobenzoic acid, 251
Paracarbonylorthophosphoric acid, 332
Paracarbonylphenylphosphoryl chloride, 332
Parachlorobenzaldehyde, 144
Parachlorobenzoic acid, 9, 221
Parachlorobenzoic acid, 221
Parachlorobenzyl acetate, 101
Parachlorobenzyl alcohol, 99, 100
Parachloro-benzylamine, 118
Parachlorobenzyl bromide, 101
Parachlorobenzyl chloride, 100
Parachlorobenzyl ethyl ether, 100
Parachlorobenzyl hydrosulphide, 106
Parachlorometacresol methyl ether, 32
Parachlorometatoluene, 19
Parachlororthonitrotoluene, 19
Parachlorotoluene, 9
Paracresol, 23, 24, 25, 28
Paracresyl benzoate, 164
Paracresyl oxide, 28
Paradiamidobenzylamine, 120
Paradiazo-amidobenzoic acid, 263
Paradiazobenzoic acid nitrate, 262
Paradichloro-benzylamine, 118
Paradihydroxybenzaldehyde, 349
Paradihydroxybenzoic acid, 361
Paradi-iodo-benzylamine, 118
Paradinitrobenzylamine, 119
Para-ethoxybenzoic acid, 330
Parafluorhippuric acid, 227
Parafluorbenzoic acid, 226
Parahomometahydroxybenzoic acid, 425
Parahomosalicylaldehyde, 422
Parahomosalicylic acid, 423
Parahydrazobenzoic acid, 266
Parahydrazotoluene, 76
Parahydroxybenzaldehyde, 294
Parahydroxybenzaldoxime, 296
Parahydroxybenzamide, 333
Parahydroxybenzanilide, 333
Parahydroxybenzide, 332
Parahydroxybenzoates, 328
Parahydroxybenzoic acid, 108
Paradroxybenzoic acid, 326; substitution products of, 334
Parahydroxybenzonitril, 334
Parahydroxybenzoylparahydroxy-benzoic acid, 331
Parahydroxybenzoyl sulphuric acid, 336
Parahydroxybenzuric acid, 333
Parahydroxybenzyl acetate, 284
Parahydroxybenzyl alcohol, 283
Parahydroxybenzyl methyl ether, 284
Parahydroxybenzyl thio-carbimide, 284
Parahydroxymetatoluic acid, 427
Parahydroxymetatolualdehyde, 422
Parahydroxymethylbenzoic acid, 442
Parahydroxymethylsalicylic acid, 490
Parahydroxyorthotolualdehyde, 422
Parahydroxyorthotoluic acid, 426
Parahydroxyphenylacetonitril, 284
Para-iodobenzaldehyde, 146
Para-iodobenzoic acid, 225

Para-iodobenzyl alcohol, 102
Para-iodo-benzylamine, 118
Para-iodobenzyl bromide, 102
Para-iodotoluene, 13
Paraleucaniline, 148
Paraleucotoluidine, 77
Paramethoxybenzoic acid, 329
Paramethoxybenzylamine, 284
Paramethoxybenzyl chloride, 284
Paramethyl-β-resorcylic acid, 360
Paramethoxysalicylaldehyde, 349
Paramidobenzaldehyde, 150
Paramidobenzaldoxime, 150
Paramidobenzamide, 253
Paramidobenzanitril, 253
Paramidobenzoic acid, 253
Paramidobenzoic acid hydrochloride, 253
Paramidobenzylphenylamine, 120
Paramidodiazobenzoic acid, 263
Paramidophthalide, 446
Paranitrobenzaldehyde, 148
Paranitrobenzaldoxime, 149
Paranitrobenzamide, 232
Paranitrobenzidene bromide, 148
Paranitrobenzidene chloride, 148
Paranitrobenzoic acid, 232
Paranitrobenzonitril, 233
Paranitrobenzoyl chloride, 232
Paranitrobenzyl acetate, 104
Paranitrobenzyl alcohol, 99, 103
Paranitrobenzylamines, 119
Paranitrobenzyl bromide, 99, 103
Paranitrobenzyl chloride, 103
Paranitrobenzyl hydrosulphide, 106
Paranitrobenzyl iodide, 103
Paranitrobenzyl nitrate, 103
Paranitrobenzyl oxalate, 104
Paranitrobenzyl thiocyanate, 123
Paranitrobenzylyphenylamine, 119
Paranitro-diamidotriphenylmethane, 148
Paranitrohippuric acid, 233
Paranitrohydroxymethylbenzoic acid, 446
Paranitromethylmetahydroxybenzaldehyde, 294
Paranitrotoluene, 15, 16
Paranitro-orthotoluidine, 69
Paranitrophthalide, 445
Para-orsellinaldehyde, 427
Para-orsellinic acid, 436, 438
Paraphenoxybenzoic acid, 331
Paraphosphorsellinic acid, 436
Pararosaniline, 148
Pararosotoluidine, 77
Parasulphamidobenzoic acid, 273
Parasulphamido-orthotoluic acid, 416
Parathiocresol, 31
Paratolualdehyde, 413
Paratoluamide, 419
Paratoluylenediamine, 73
Paratoluic acid, 418
Paratoluidine, 63
Paratoluidine hydrobromide, 64
Paratoluidine hydrochloride, 64
Paratoluidine nitrate, 64
Paratoluidine phenate, 64
Paratoluidine sulphate, 64
Paratolunitril, 420
Paratoluylamido-acetic acid, 419
Paratoluyl chloride, 419
Paratolylbenzoyl thio-urea, 179
Paratolylboron chloride, 87
Paratolyl carbamide, 66
Paratolylhydrazine, 75
Paratolyl mustard oil, 67
Paratolylphosphenilic acid, 83
Paratolylphosphenylous acid, 83
Paratolylphosphine, 84
Paratolylphosphonium iodide, 84
Paratolylphosphorus dichloride, 83
Paratolylphosphorus oxychloride, 83
Paratolylphosphorus tetrachloride, 83
Paratolylsilicic acid, 87
Paratolylsilicon chloride, 87
Paratolylsilicon oxide, 87
Paratolylstibine, 86
Paratolylstibine bromide, 86
Paratolylstibine chloride, 86
Paratolylstibine hydroxide, 86
Paratolylstibine iodide, 86
Paratolylstibine oxide, 86
Paratolyl thiocarbamide, 67
Paratolyl thiocarbimides, 67
Paratolyl urethane, 67
Paratriamidobenzylamine, 120
Paratribromo-benzylamine, 118
Paratrichloro-benzylamine, 118
Paratri-iodo-benzylamine, 118
Paratrinitrobenzylamine, 119
Para-uramidobenzoic acid, 254
Paraxylyl alcohol, 412
Paraxylenol, 401
Paraxylene, 388, 389, 391
Paraxylenesulphamide, 399
Paraxylenesulphonic acid, 399
Paraxylenesulphonic chloride, 399
Paraxylidine, 407
Paraxylidene tetrachloride, 448
Paraxyloquinol, 403
Paraxyloquinone, 404
Paraxylorcinol, 402
Paraxylylene acetate, 441
Paraxylylene alcohol, 441
Paraxylyl bromide, 412
Paraxylylene bromide, 441
Paraxylylene chloride, 441
Paraxylylene iodide, 441
Paraxylylene monobenzoate, 442
Paraxylylene mono-ethyl ether, 441
Paraxylyl ethyl ether, 412
Parazobenzoic acid, 266
Penta-acetyltannin, 374
Pentabromobenzoic acid, 225
Pentabromorcinol, 41
Pentabromotoluene, 12
Pentachlorobenzidene chloride, 8, 145

Pentachlorobenzyl alcohol, 100
Pentachlorobenzyl chloride, 101
Pentachlororcinol, 41
Pentachlorotoluene, 10
Pentachloroxylone, 34
Persio, 44
Peruvin, 90
Petrol, 387
Phenol, 297
Phenylacetamide, 113
Phenylacetonitril, 113
Phenylaceturic acid, 186
Phenylamido-acetonitril, 113
Phenylbenzaldehydine, 141
Phenylbenzaldehydine hydrochloride, 141
Phenylbenzenylamidine, 203
Phenyl benzoate, 163
Phenylbenzoyl thio-urea, 179
Phenylchlorocarbylethyl ether, 100
Phenylchloroform, 195
Phenylene benzoate, 164
Phenylenebenzenylamidine, 205
Phenylenediethylacetone, 462
Phenylenenitrobenzenylamidine, 206
Phenylhydrazine nitro-opianic acid, 508
Phenylhydroxyacetic acid, 132
Phenylhydroxyacetonitril, 113, 131
Phenyl isophthalate, 480
Phenylorthotolylamine, 59
Phenylmetabenzoglycocyamine, 252
Phenylmethyl, 89
Phenyl methylsalicylate, 308
Phenylnitro-ethylene, 135
Phenylorthotolyl thiocarbamide, 60
Phenyl paraphenoxybenzoate, 331
Phenyl parahydroxybenzoate, 330
Phenyl paratoluate, 419
Phenylparatoluidine, 65
Phenylparatolylamine, 65
Phenylphthalimide, 464
Phenylphthalimidine 445
Phenylpropionic acid, 186
Phenylpropionitril, 122
Phenyl salicylate, 307
Phenyl terephthalate, 484
Phenylthiobenzamide, 178
Phenylthiobenzoate, 171
Phloroglucinol, 357
Phloroglucinolcarboxylic acid, 380, 381
Phlorone, 404
Phosphorsellinanilide, 433
Phosphorsellinic acid, 433
Phosphorus compounds of benzyl, 124
Phosphorus derivatives of toluene, 83
Phosphorus pentachloride and its action upon salicylic acid, 309
Phospho-salicylic acid, 309
Phthalalcohol, 439
Phthalaldehyde, 442, 447
Phthalaldehydic acid, 447
Phthalamic acid, 463
Phthalamil, 464
Phthalanilic acid, 464
Phthaleïns, 458
Phthalic acid, 439, 451, 452
Phthalic acid, addition products of, 469
Phthalic acid, halogen substitution products of, 471
Phthalic acids, 450
Phthalic anhydride, 457 ; apparatus for the sublimation of, 459
α-Phthalicsulphamic acid, 477
Phthalide, 442, 458
Phthalide-anil, 445
Phthalidehydrazide, 445
Phthalimide, 463
Phthalimide oxime, 469
Phthalimidine, 444
Phthalinic acid, 464
Phthalylacetic acid, 458
Phthalyl chloride, 458
Phthalyldiamide, 466
Phthalylhydroxylamine, 466, 468
Phthalyloxide, 457
Phthalyl sulphide, 462
Picranyl, 129
Picroerythrin, 429, 431, 434
Picrorocellin, 436
Piperonal, 347
Piperonic acid, 355
Piperonyl alcohol, 347
Polysalicylnitril, 313
Pomaceæ, 131
Populin, 282, 317
Potassium benzidene sulphite, 137
Potassium benzoate, 160
Potassium benzylsulphonate, 108
Potassium chlorobenzylsulphonate, 108
Potassium cyanate, 518
Potassium dibenzhydroxamate, 210
Potassium dinitroparacresate, 31
Potassium dinitrosalicylate, 317
Potassium gallate, 368
Potassium hemipinimide, 513
Potassium hippurate, 189
Potassium hydroxyphthalamate, 467
Potassium isophthalate, 479
Potassium opianate, 504
Potassium parahydroxybenzoate, 328
Potassium phthalimide, 463
Potassium piperonate, 356
Potassium salicylaldehyde, 287
Potassium salicylate, 302
Potassium thiobenzoate, 170
Potassium α-toluquinonoximate, 51
Potassium tribenzarsenate, 278
Proin, 128
Propenyl salicylate, 306
Propyl benzoate, 162
Propylene, 24
Propylene benzoate, 163
Propyl salicylate, 306
Propyl terephthalate, 484
Protocatechuic acid, 350, 357

Protocatechuicaldehyde, 343
Protonitrobenzoine, 13
Pseudoerythrin, 428
Pseudotoluidine, 55
Pyrogallocarboxylates, 379
Pyrogallolcarboxylic acid, 378, 381

Q.

QUERCIMERIC acid, 509
Quinates, the, 384
Quinic acid, 186, 381
Quinoldicarboxylic acid, 515, 518
Quinonedihydrodicarboxylic acid, 518
Quinonoxime benzoate, 165

R.

RESORCINOLDICARBOXYLIC acid, 515
β-Resorcylaldehyde, 348
α-Resorcylic acid, 358
β-Resorcylic acid, 359, 437
γ-Resorcylic acid, 360
Retinaphtha, 3
Ribbon Litmus, 46

S.

SACCHARIN, 269
Safranine, 80
Salicin, 281
Salicyl, 285
Salicyl alcohol, 279
Salicylaldehyde, 285 ; properties, 286
Salicylaldehyde, substitution products of, 292
Salicylaldoxime, 290
Salicylamide, 312
Salicylates, 301
Salicyl chloraldide, 308
Salicyl chloride, 310
Salicyl hydride, 285
Salicylhydroxyacetic acid, 309
Salicylic acid, 108, 157, 297
Salicylic acid, ethereal salts of, 306
Salicylic acid, substitution products of, 313
Salicylic ethers, 306
Salicylic ethers, ethereal salts of, 307
Salicylide, 308
Salicyl monochlorophosphate, 309
Salicylnitril, 313
Salicylparazobenzenesulphonic acid, 319
Salicylsulphuric acid, 319
Salicyluric acid, 312
Saligesion, 279
Saliretin, 280
Salireton, 280
Salol, 307
Salts and ethers of benzoic acid, 160
Selenium compounds of benzyl, 109
Silicon compounds of benzyl, 127
Silicon paratolyl, 87
Silicon tetrabenzyl, 127
Silicotetrabenzylmethane, 127
Silver benzarsenate, 277
Silver benzarsenite, 278
Silver benzoate, 161
Silver benzophosphinate, 276
Silver hemipinimide, 513
Silver hippurate, 190
Silver isophthalate, 479
Silver metasulphobenzoate, 270
Silver methylnoropianate, 503
Silver opianite, 504
Silver orthohydroxymethylbenzoate, 442
Silver parahydroxybenzoate, 328
Silver phthalate, 457
Silver phthalimide, 463
Silver piperonate, 356
Silver quinate, 384
Silver salicylate, 304
Silver terephthalate, 484
Sinalbin, 377
Sinapic acid, 376
Sinapin, 375
Sinapin thiocyanate, 375
Sodium arsenetribenzoate, 278
Sodium benzidene sulphite, 137
Sodium benzoate, 160
Sodium gallate, 368
Sodium hippurate, 189
Sodium metanitrobenzoate, 231
Sodium metaxylenesulphonate, 398
Sodium orthoxylenesulphonate, 398
Sodium parahydroxybenzoate, 328
Sodium paraxylenesulphonate, 399
Sodium phenylenecarbonate, 299
Sodium quinate, 384
Sodium salicylate, 302
Sodium tetrahydroxyterephthalate, 520
Sodium a-toluquinonoximate, 51
Spiræic acid, 285
Spiroyl hydride, 285
Spiroylous acid, 285
Spiroylwasserstoffsäure, 285
Strontium hippurate, 189
Substitution products of benzyl alcohol and its derivatives, 98
Substitution products of anisic acid, 336
Substitution products of benzidene compounds, 143
Substitution products of benzylamines, 118
Substitution products of isophthalic acid, 481
Substitution products of metahydroxybenzoic acid, 323
Substitution products of parahydroxybenzoic acid, 334
Substitution products of salicyl-aldehyde, 292

Substitution products of salicylic acid, 313
Substitution products of terephthalic acid, 488
Substitution products of the xylenes, 392
Sulphamicphthalic anhydride, 477
Sulphamidobenzonitril, 272
α-Sulphamidometatoluic acid, 418
v-Sulphamidometatoluic acid, 418
Sulphamidoparatoluic acid, 421
Sulphinidephthalic acid, 477
Sulphobenzoic acid, 20
Sulphobenzoyl hydride, 138
α-Sulpho-isophthalic acid, 482
s-Sulpho-isophthalic acid, 482
Sulphometahydroxybenzoic acid, 325
Sulphoparahydroxybenzoic acid, 335
Sulphoparatoluic acid, 421
α-Sulphophthalic acid, 476
v-Sulphophthalic acid, 477
Sulphophthalic acids, 476
Sulphorthotoluic acid, 415
Sulphosalicylic acid, 318
Sulphoterephthalic acid, 490
Sulphur compounds of benzoyl, 170
Sulphur compounds of benzyl, 105
Symmetric α-diamido-azotoluene, 79
Symmetric β-diamido-azotoluene, 79
Symmetric dibenzyl thiocarlamide, 124
Symmetric dibenzyl urea, 123
Symmetric dinitroparatoluidine, 71
Symmetric diphenylbenzenylamidine, 203
Symmetric ethylbenzoyl urea, 178
Symmetric metadihydroxybenzoic acid, 358

T.

Tannates, 374
Tannic acid, 365, 371
Tannin, 371 ; properties, 373
Tartrophthalic acid, 470
Taurylic acid, 23
Telerythrin, 428
Terephthalaldehyde, 447
Terephthalaldehydic acid, 449
Terephthalamic acid, 485
Terephthalamide, 485
Terephthalic acid, 451, 483 ; addition products of, 486 ; substitution products of, 488
Terephthalonitril, 485
Terephthalyl chloride, 485
Tetrabromolecanoric acid, 434
Tetrabromometaxylene, 394
Tetrabromomethane, 12
Tetrabromoparaxylene, 395
Tetrabromophthalic acid, 473
Tetrabromorthoxylene, 394
Tetrabromoluenes, 12
Tetracetylhelicin, 289
Tetrachlorobenzal chloride, 8
Tetrachlorobenzidene chloride, 145
Tetrachlorobenzoic acid, 222
Tetrachlorobenzyl alcohol, 100
Tetrachlorobenzyl chloride, 101
Tetrachlorobenzenyl trichloride, 196
Tetrachlorocreocone, 36
Tetrachloroguaiacone, 36
Tetrachlorophthalic acid, 472
Tetrachlororthoxylene, 393
Tetrachlorotoluene, 10
Tetrachlorotoluquinone, 50
Tetrahydro-isophthalic acid, 481, 487
Tetrahydrometaxylene, 391
Tetrahydrophthalic acid, 470
Tetrahydroterephthalic acid, 486
Tetrahydrotoluene, 6
Tetrahydroxyhexhydrobenzoic acid, 383
Tetrahydroxyphthalic acids, 519
Tetrahydroxyterephthalic acid, 519
Tetrasalicylide, 308
Thallium metahydroxybenzoate, 321
Thallium salicylate, 303
Thiobenzaldine, 140
Thiobenzamide, 177
Thiobenzanilide, 178
Thiobenzoic acid, 170
Thiobenzoic anhydride, 171
Thiocresolo, 31
Thiometahydroxybenzoic acid, 325
Thio-opianic acid, 507
Thiophthalic anhydride, 462
Thiotoluidine, 72
Tolualdehydes, the, 413
Tolubenzaldehydine, 142
Toluene 3 *et seq.*, properties, 5
Toluene, amido-derivatives of, 54
Toluene, antimony derivatives of, 86
Toluene, arsenic derivatives of, 84
Toluene, azo-derivatives of, 75
Toluene, boron and silicon derivatives of, 87
Toluene, diazo-derivatives of, 74
Toluenedisulphonic acids, 22
α-Toluenedisulphonic acid, 22
β-Toluenedisulphonic acid, 22
γ-Toluenedisulphonic acid, 22
Toluene group, 3
Toluene, hydrazine derivatives of, 75
Toluene, mercury derivatives of, 87
Toluene, phosphorus derivatives of, 83
Toluenemetasulphonamide, 21
Toluenemetasulphonic acid, 21
Toluenemetasulphonic chloride, 21
Toluenemonosulphonic acids, 20
Tolueneparasulphonamide, 21
Tolueneparasulphonic acid, 21
Tolueneparasulphonic chloride, 21
Toluene-orthosulphonic acid, 21
γ-Toluenesulphonic acid, 22
Toluenesulphonic acids, 20
Toluenetrisulphonic acids, 22
Toluenyl alcohol, 412
Toluhydroquinone, 48

Toluic acids, 414
Toluidine, 4, 14, 111
Toluidinedisulphonic acid, 22
Toluidines, 54
Toluidines, halogen substitution products of the, 67
Toluol, 386
Toluquinhydrone, 50
Toluquinol, 48
Toluquinol dimethyl ether, 48
Toluquinol monomethyl ether, 48
Toluquinone, 49
α-Toluquinone chlorimide, 51
Toluquinone, substitution products, 50
α-Toluquinonoxime, 50
β-Toluquinonoxime, 51
β-Toluquinonoxime acetate, 51
Toluquinonoxime compounds, 50
Toluric acid, 419
Tolusafranine, 80
Tolusafranine hydrochloride, 81
Tolusafranine nitrate, 81
Tolusafranine picrate, 81
Toluylene-blue, 82
Toluylene-red, 82
Toluylene-violet, 82
Tolyl, 410
Tolylarsenic acid, 85
Tolylboric acid, 87
Tolylenediamines, 72
Triacetoxymetaxylene, 403
Triacetylgallic acid, 370
Triamido-azobenzoic acid, 264
Tri-amidobenzoic acid, 260
Triamidometaxylene, 409
Tribenzhydroxylamine, 207
Tribenzhydroxylamine, 211
α-Tribenzhydroxylamine, 212
β-Tribenzhydroxylamine, 212
γ-Tribenzhydroxylamine, 212
Tribenzidenediamine, 139
Tribenzo-arsenic acid, 85
Tribenzoylphloro-glucinol, 164
Tribenzylamine, 110, 115
Tribenzylamine, hydrochloride, 116
Tribenzylamine nitrate, 116
Tribenzylamine sulphate, 116
Tribenzylarsine, 126
Tribenzylarsine dichloride, 125
Tribenzylarsine oxide, 126
Tribenzarsenic acid, 278
Tribenzarsenious acid, 278
Tribenzylarsonium iodide, 126
Tribromobenzoic acids, 225
α-Tribromometaxylenol, 401
s-Tribromometaxylenol, 401
ν-Tribromometaxylenol, 401
Tribromoparaxylenol, 401
Tribromophthalic acid, 473
Tribromorcinol, 41
α-Tribromorthoxylenol, 400
Tribromotoluenes, 12
Tribromotoluquinone, 50
α-Trichlorobenzaldehyde, 145
β-Trichlorobenzaldehyde, 145
α-Trichlorobenzidene chloride, 145
β-Trichlorobenzidene chloride, 145
α-Trichlorobenzoic acid, 222
β-Trichlorobenzoic acid, 222
γ-Trichlorobenzoic acid, 222
Trichlorobenzoic acids, 222
Trichlorobenzyl alcohol, 100
Trichlorobenzyl chloride, 101
Trichlorobenzenyl trichloride, 196
Trichlorophthalic acid, 472
Trichlororcinol, 41
Trichlororthoxylene, 393
α-Trichlorotoluene, 10
β-Trichlorotoluene, 10
Trichlorotoluquinone, 50
Triethyl benzylammonium iodide, 116
Triethylgallic acid, 369
Triethylhydroxyquinolcarboxylic acid, 380
Triethylpyrogallolcarboxylic acid, 379
Trihydroxybenzoic acids, 363
Trihydroxybenzoic acids, constitution of, 381
Trihydroxymetaxylene, 403
Trihydroxyphthalic acids, 519
Trihydroxytoluenes, 53
Trihydroxy-xylenes, 403
Tri-iodorcinol, 41
Tri-iodosalicylic acid, 315
Triketohexhydrobenzene, 518
Trimethylamido-anisic acid, 338
Trimethylamidobenzoic acid, 248
Trimethylamidosalicylic acid, 318
Trimethyl anise-betaïne, 338
Trimethylene benzoate, 163
Trimethyl ether, 478
Trimethylhydroxyquinolcarboxylic acid, 380
Trimethylorthotolylammonium iodide, 59
Trimethylparatolylammonium iodide, 65
Trimethylphosphobenzobetaïne, 276
Trinitro-amarine, 148
Trinitrobenzene, symmetric, 18
Trinitrobenzoic acid, 235
Trinitrohydrobenzamide, 148
Trinitrometahydroxybenzoic acid, 324
s-Trinitrohydroxytoluic acid, 425
Trinitrometacresol, 28
Trinitrometaxylene, 396
Trinitroparaxylene, 398
Trinitrophenyl benzoate, 164
Trinitro-orcinol, 42
Trinitro-orthoxylene, 396
α-Trinitrotoluene, 17
β-Trinitrotoluene, 18
γ-Trinitrotoluene, 18
Trinitrotoluenes, 17
Triopianide, 505
Triparatolylarsine, 85
Triphenylbenzylphosphonium chloride, 125

Trisulphometahydroxybenzoic acid, 326
Trixylylamine, 413
Tuluol, 4

U.

UMBELLIC ACID, 329
Uramidobenzoic acid, 249, 252
Uramidobenzoyl, 242
Uronitrotoluic acid, 104

V.

VANILLA, 345
Vanillic acid, 352
Vanillic acid glucoside, 352
Vanillin, 344
Vanillin glucoside, 347
Vanillyl alcohol, 346
Veratric acid, 354
Victoria yellow, 31

X.

XANTHAROCELLIN, 436
Xylene group, 386
Xylenes, 390
Xylenes, amido-derivatives of the, 405
Xylenes, diamines and triamines of the, 409
Xylenes, halogen substitution products of the, 392
Xylenes, nitro substitution products of the, 395
Xylenes, substitution products of the, 392
Xylenesulphonic acids, 398
Xylenols, 399
Xylidenyl pentachloride, 447
Xylidines, 405
Xylol, 386
Xyloquinones, the, 404
Xyloylamines, 412
Xylyl, 410
Xylyl alcohols, 411
Xylyl bromides, 412
Xylyl chlorides, 412
Xylyl compounds, 410
Xylylene alcohols, 439
Xylylidenediamine, 448

Z.

ZINC HIPPURATE, 189
Zinc phthalate, 458

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